

CHEMICAL- AND ELECTRONIC-STATE CHARACTERIZATION OF THE
SURFACE REGION OF METALS
FOLLOWING CHEMISORPTION OF SIMPLE GASES
USING ELECTRON BEAM SPECTROSCOPIES

By

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TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	xi
CHAPTERS	
I GENERAL INTRODUCTION.....	1
II AN ELECTRON-ENERGY-LOSS STUDY OF CLEAN AND OXYGEN-EXPOSED POLYCRYSTALLINE ZIRCONIUM.....	5
Introduction.....	5
ELS Background.....	9
Experimental Procedure.....	13
ELS Results and Discussion.....	17
Clean polycrystalline zirconium.....	17
Oxygen-exposed zirconium.....	23
Conclusions.....	32
III AN INTERPRETATION OF ELS SPECTRA FROM POLYCRYSTALLINE ZIRCONIUM SURFACES AFTER EXPOSURE TO H ₂ AND H ₂ /O ₂	34
Introduction.....	34
Experimental Procedure.....	36
Results and Discussion.....	38
Hydrogen-exposed zirconium.....	38
Hydrogen-exposed/oxygen-exposed zirconium.....	48
Conclusions.....	53
IV OXYGEN UPTAKE AND CO ADSORPTION ON POLYCRYSTALLINE ZIRCONIUM.....	54
Introduction.....	54
Experimental Procedure.....	55
Results and Discussion.....	56
Oxygen uptake experiments.....	56
CO adsorption.....	60
Conclusions.....	64

	PAGE
V	AN ELECTRON-ENERGY-LOSS STUDY OF CLEAN AND OXYGEN-EXPOSED POLYCRYSTALLINE TIN..... 65
	Introduction..... 65
	Experimental Procedure..... 68
	Results and Discussion..... 69
	ELS Depth Sensitivity..... 69
	Clean polycrystalline tin..... 70
	Oxygen-exposed polycrystalline tin..... 80
	Loss spectra interpretation..... 82
	Oxidation state depth profile..... 95
	Conclusions..... 101
VI	AN ENERGY-RESOLVED ELECTRON STIMULATED DESORPTION (ESD) STUDY OF OXYGEN-EXPOSED Ag(110)..... 104
	Introduction..... 104
	Experimental Procedure..... 106
	Results and Discussion..... 108
	Conclusions..... 122
VII	GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH..... 124
	REFERENCES..... 129
	BIOGRAPHICAL SKETCH..... 136

LIST OF TABLES

TABLE		PAGE
2-1.	Clean Zirconium ELS Assignments.....	19
2-2.	Partially Oxidized Zirconium ELS Assignments.....	27
3-1.	Occupied Energy Level Peak Positions for Hydrogen-exposed Zirconium.....	41
3-2.	Hydrogen-exposed Zirconium ELS Assignments.....	42
5-1.	ELS Sampling Depths for Clean Tin.....	75
5-2.	ELS Sampling Depths for SnO.....	87

FIGURE	LIST OF FIGURES	PAGE
2-1.	AES spectrum taken from a polycrystalline zirconium surface cleaned by repeated sputtering and annealing at 1500 K.....	14
2-2.	AES spectrum taken after an exposure to 40 L of oxygen at 300 K.....	16
2-3.	ELS spectra taken from the zirconium surface shown in figure 2-1 using primary beam energies of 100, 150, 300, 400 and 600 eV. Loss features are designated according to the mechanisms believed to be responsible. The peak assignments are summarized in Table 2-1 and in the text.....	18
2-4.	Occupied and unoccupied energy levels of zirconium obtained from the ELS spectra and other sources (see text). The electronic transitions larger than 4 eV are depicted, and the transitions are labelled as in figure 2-3.....	22
2-5.	ELS spectra taken from the oxygen-exposed zirconium surface shown in figure 2-2 using primary beam energies of 100, 200, 400 and 600 eV. Loss features are designated according to the loss mechanisms believed to be responsible. The peak assignments are summarized in Table 2-2 and in the text.....	25
2-6.	Enlargement of low energy-loss region of the ELS spectra shown in figure 2-5.....	26
2-7.	Occupied and unoccupied energy levels of zirconium dioxide obtained from ELS spectra and other sources (see text). The electronic transitions larger than 3 eV are depicted, and the transitions are labelled as in figure 2-5.....	30

3-1.	ELS spectra taken from the clean surface following a dose of 2000 L of hydrogen at 770 K using primary beam energies of 100, 150, 200, 400 and 600 eV. Loss features are designated according to the mechanism believed to be responsible and are given in Table 3-2.....	39
3-2.	ELS spectra obtained using primary beam energies of (a) 600 eV, (b) 150 eV and (c) 100 eV. The dashed-line spectra are from the cleaned surface, and the solid-line spectra are from the hydrogen-exposed surface.....	45
3-3.	ELS spectra obtained using primary beam energies of (A) 200 eV and (B) 600 eV. The dashed-line ELS spectra were taken from a 40 L oxygen-exposed surface, and the solid-line ELS spectra were taken from a 2000 L hydrogen pre-exposed, 40 L oxygen-exposed surface.....	49
3-4.	Enlargement of the low-energy-loss region of ELS spectra obtained from (A) the 40 L oxygen-exposed and (B) the 2000 L hydrogen-pre-exposed, 40 L oxygen-exposed surfaces. The spectra were obtained using primary beam energies of 100, 200, 400 and 600 eV. The spectra from the 40 L oxygen-exposed surface are reproduced from reference 65.....	52
4-1.	Oxygen uptake as a function of room-temperature oxygen exposure as determined by (a) ISS, (b) AES and (c) XPS. The O/Zr peak-height ratio is plotted in (a), the O (515 eV)/Zr (92 eV) peak-height ratio is plotted in (b) and the O 1s/Zr 3d peak-area ratio is plotted in (c). The ordinate scale is indicated for the ISS results. The XPS and AES scales are 2 and 4 times these values respectively, but the scaling of the curves with respect to each other is arbitrary.....	57
4-2.	AES spectrum taken after exposing the clean zirconium surface to 2500 L of CO at room temperature.....	61

4-3.	ISS spectrum corresponding to the AES spectrum shown in figure 4-2.....	62
4-4.	ELS spectra obtained from polycrystalline zirconium following a 4000 L exposure of CO. The primary beam energies used are 100, 200, 400 and 600 eV.....	63
5-1.	An AES spectrum of sputter cleaned polycrystalline tin.....	71
5-2.	ELS spectra taken from sputter cleaned polycrystalline tin using primary beam energies of 200, 400 and 600 eV.....	72
5-3.	Angle-resolved ELS spectra taken from sputter cleaned polycrystalline tin. Spectra (a) and (b) were obtained with $E_p = 200$ eV, and spectra (c) and (d) were obtained with $E_p = 600$ eV. Spectra (a) and (c) were obtained with $X = 80$ degrees and $Y = 80$ degrees, and spectra (b) and (d) were obtained with $X = 80$ degrees and $Y = 0$ degrees.....	74
5-4.	A $E_p = 100$ eV ELS spectrum taken from sputter cleaned polycrystalline tin.....	79
5-5.	Standard ELS spectra for sputter cleaned polycrystalline tin, SnO and SnO ₂ , taken using a 400 eV primary beam. This spectra has been reproduced from Powell (87).....	81
5-6.	ELS spectra obtained from 100 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.....	83
5-7.	ELS spectra obtained from 500 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.....	84
5-8.	ELS spectra obtained from 1500 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.....	85
5-9.	ELS spectra obtained from 3500 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.....	86

5-10.	$E_p = 200$ eV ELS spectra obtained from the cleaned surface and from polycrystalline tin following oxygen exposures of 100, 500, 1500 and 3500 L.....	88
5-11.	$E_p = 600$ eV ELS spectra obtained from the cleaned surface and from polycrystalline tin following oxygen exposures of 100, 500, 1500 and 3500 L.....	89
5-12.	$E_p = 200$ eV angle-resolved ELS spectra obtained from polycrystalline tin following a 3500 L oxygen dose. The incident and collected beam angles are labelled.....	92
5-13.	$E_p = 100$ eV ELS spectra obtained from the cleaned surface and polycrystalline tin following oxygen exposures of 50, 100 and 500 L.....	94
5-14.	ISS spectra obtained from sputter cleaned polycrystalline tin, 3000 L oxygen-exposed tin and air-exposed tin. This data has been reproduced from Asbury and Hoflund (94).....	96
5-15.	ELS spectra obtained from polycrystalline tin following an oxygen exposure of 160 Torr for 5 minutes. The primary beam energies used are 100, 200, 400 and 600 eV.....	99
5-16.	ELS spectra obtained from polycrystalline tin following air exposure for 5 minutes. The primary beam energies used are 100, 200, 400 and 600 eV.....	100
5-17.	An ELS semiquantitative depth profile of sputtered polycrystalline tin as a function of oxygen exposure.....	102
6-1.	An ISS spectrum taken from the cleaned silver surface.....	109
6-2.	A typical AES spectrum taken from the cleaned silver surface.....	111

- 6-3. Total ion energy distributions obtained during the initial oxygen exposures. From spectrum (a) to (c) the subsurface oxygen concentration is increasing. A primary beam energy of 300 eV was used to obtain these spectra. The ordinates are not scaled relatively to each other..... 112
- 6-4. ESD mass spectra obtained from Ag(110) following the initial oxygen exposures. Spectrum (a) was obtained by collecting ions with an energy of 3.2 eV, and spectrum (b) was obtained by collecting ions with an energy of 4.7 eV. The ordinates are not scaled relatively to each other..... 114
- 6-5. Time-gated energy distributions for (a) OH^+ and (b) H^+ 115
- 6-6. Total ion energy distribution curves. Spectrum (a) was obtained following the initial oxygen exposures and an additional 7500 L. Spectrum (b) was obtained following prolonged exposure to the electron beam. Spectrum (c) was obtained by annealing the surface at 625 K. The ordinates are scaled as shown..... 117
- 6-7. Mass spectra of ions collected with an energy of 4.7 eV as a function of oxygen exposure: (a) 250 L, (b) 500 L and (c) 1000 L. The ordinates are not scaled relatively to each other..... 119
- 6-8. Total ion energy distributions obtained successively with primary beam energies of (a) 300, (b) 400 and (c) 300 eV. The ordinates are scaled such that (b) has been expanded by a factor of two..... 120

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The initial adsorption of oxygen on a polycrystalline zirconium surface was followed by using ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Based on the results from these three spectroscopies, it is determined that the adsorption of oxygen proceeds by first populating some of the outermost binding sites followed by transport of oxygen into the subsurface region. Moreover, before the surface binding sites are saturated and following an exposure of approximately $3/4$ of a Langmuir ($1 \text{ Langmuir} = 1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{sec.}$), most of the oxygen which adsorbs migrates into and oxidizes the subsurface region.

Electron energy loss spectroscopy (ELS) has also been used to study an oxygen-exposed zirconium surface. Depth-sensitive oxidation state information is obtained by varying the primary electron beam energy from 100 to 600 eV. The oxidation state of the zirconium is

found to increase with depth through the surface region, and evidence is found which suggests that suboxides such as ZrO , Zr_2O_3 and possibly nonstoichiometric oxides are present.

Additionally, the interaction of hydrogen with zirconium has been studied using ELS. ELS is found to be sensitive to hydrogen throughout the surface region. Following a 2000 L dose of hydrogen at 770 K ELS spectra have been obtained and interpreted. Also, by varying the primary beam energy a depth profile of the hydrided layer is obtained.

ELS has also been used to study the oxygen-tin interaction. Following a low-pressure saturation oxygen exposure roughly a 2 nm oxide layer approximated by SnO is formed on a polycrystalline surface. Following high pressure exposures a broad mixture of oxidation states is present throughout the surface region. Lower oxidation states appear to dominate; however, some SnO_2 is observed and is at a maximum near 1.5 nm in depth.

The interaction of oxygen with the $\text{Ag}(110)$ surface has been studied using electron stimulated desorption (ESD). Adsorbed oxygen on the $\text{Ag}(110)$ surface predominately desorbs by ESD as a hydroxyl ion. Two or more possible binding sites for oxygen exist on the $\text{Ag}(110)$ surface and exciting the Ag 3d core levels results in a dramatic variation in the desorption yields for OH^+ and H^+ .

CHAPTER I GENERAL INTRODUCTION

The chemical and electronic state characterization of the surface region of metals following adsorption of simple gases is important in a wide variety of materials research from catalysis and corrosion research to semiconductor device fabrication research. To a large extent the important characteristics of many materials are derived from the surface region of the material, that is, the region comprising approximately the 10 outermost atomic layers. This region of materials is not well understood, and from analytical and/or constitutive expressions it is not yet possible to derive or predict surface properties. Furthermore, it is not possible presently to predict the effect on surface properties of either adsorption of simple gases or of surface modification (e.g. varying surface roughness). Also, it is not possible to predict the adsorption characteristics of a particular surface. Thus, the only viable alternative for understanding material surfaces is to use experimental techniques.

In performing experiments it is advantageous to limit the number of variables involved in any particular experiment. An obvious method for limiting the number of variables in surface studies is to remove any background interactions that might be taking place by performing the experiments in vacuum. Moreover, by performing the experiments in vacuum the mean free path of photons, electrons and atoms is increased such that many powerful surface sensitive

spectroscopies can be used. Unfortunately, a problem with vacuum studies is that it is not clear whether surface properties determined are representative of surface properties that occur in the working environment of the material. At present there is no definitive solution to this problem.

To characterize the chemical state or the adsorption properties of a surface using surface spectroscopies it is important to use as many different techniques as possible. This is because the different techniques are sensitive to different depths in the surface region, have differing sensitivities to different surface species and are sensitive to different electronic and/or structural properties of the surface region. It is also important to continually improve the understanding of the various spectroscopies so that data can be more reliably interpreted. The major thrust of the work presented lies in the latter of these ideas and involves, among others, the use of electron energy loss spectroscopy (ELS) to study primarily the oxidizing and hydriding behavior of various surfaces.

Electron energy loss spectroscopy is a powerful surface spectroscopy; however the interpretation of the data is difficult. The advantages of using this technique are its very high sensitivity to adsorption and chemical state changes, its relative non-destructiveness to surface species, its ease of depth profiling and its ease of performing. To utilize these advantages it is important to better understand this technique and improve the data interpretation.

The body of the dissertation has been divided up into five chapters. A brief introduction of each chapter is as follows. The first three chapters comprise three separate, independent studies concerning the interaction of oxygen, hydrogen and carbon monoxide with polycrystalline zirconium. In the first of the zirconium chapters, ELS results for zirconium metal and partially oxidized zirconium are presented for primary beam energies ranging from 100 to 600 eV. A detailed interpretation of these results is offered, and clear evidence for the presence of suboxide formation and variations in the zirconium oxidation state with depth are observed.

The second zirconium chapter comprises an ELS study of hydrogen-exposed polycrystalline zirconium which is part of an ongoing effort to understand the Zr-H, Zr-O and Zr-H-O interactions (1-4). The Zr-H and Zr-O-H interactions are difficult to study because most surface spectroscopies are relatively insensitive to hydrogen. Furthermore, there are even fewer spectroscopies which enable the detection of hydrogen beneath the outermost layer. ELS, however, is found to be sensitive to the presence of hydrogen throughout the surface region. In this chapter ELS spectra are presented for hydrogen-exposed zirconium and oxygen- and hydrogen-exposed zirconium. The primary beam energy was varied to obtain depth profiles of the surface region. These data and their interpretation form a basis for further detailed studies of the hydrogen-zirconium interaction.

The final zirconium chapter concerns a study of the interaction of oxygen and carbon monoxide with polycrystalline zirconium using ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES)

and X-ray photoelectron spectroscopy (XPS). The initial oxygen uptake is following and an oxygen adsorption process is proposed. The results of this study using these three spectroscopies and the results of the ELS study in chapter two have led to a good understanding of the oxidation of polycrystalline zirconium surface. Further, carbon monoxide adsorption has been studied and limited depth sensitive information is obtained.

The fourth chapter of the dissertation body involves an extensive and detailed ELS investigation of clean and oxygen-exposed polycrystalline tin. In this study it is demonstrated that ELS can be used to semiquantitatively depth profile the oxidation state of tin in the surface region as a function of oxygen exposure by varying the primary electron beam energy and the experimental geometry.

The final chapter of the body concerns an energy-resolved electron stimulated desorption (ESD) study of the oxidation of silver(110). This study was initiated in order to investigate the possibility of producing a hyperthermal oxygen atom-beam source using ESD. This type of source would be useful in studying collision dynamics and in materials research. In this source oxygen would diffuse from a high pressure region through a metal membrane and desorb under electron bombardment at the metal surface. Silver is a candidate for the metal membrane because oxygen readily diffuses through it (5). This work is part of an ongoing effort to obtain the information required to construct this source (5).

CHAPTER II
AN ELECTRON ENERGY LOSS (ELS) STUDY OF CLEAN
AND OXYGEN-EXPOSED POLYCRYSTALLINE ZIRCONIUM

Introduction

The oxidation of zirconium has been investigated macroscopically (6) and in a variety of surface studies (3,4,7-28). However, these studies have not yielded a clear understanding of the electronic interaction of oxygen with zirconium. Furthermore, little is known about the initial stages of oxidation or even which surface oxide(s) is (are) stable or present at room temperature.

The adsorption of oxygen on polycrystalline zirconium has been studied by Foord et al. (8) using Auger electron spectroscopy (AES), work function measurements and thermal programmed desorption (TPD). They suggest that oxygen adsorbs almost entirely dissociatively at 300 K and is immediately incorporated into the first few atomic layers of the solid. Also, by following the KLL oxygen Auger signal intensity, Foord et al. (8) determined that at 300 K a 30 L oxygen dose ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{sec}$) results in a saturation coverage. However, using this method to determine a saturation oxygen coverage for zirconium may not be accurate due to electron beam damage which affects Auger signal intensities (26). Using X-ray photoelectron spectroscopy (XPS), Tapping (7) estimates that a saturation coverage requires a 50 L dose and results in an approximate oxide layer thickness of 2.9 nm.

The energy levels of oxygen-exposed polycrystalline zirconium have been investigated using XPS and ultraviolet photoelectron spectroscopy (UPS) (7,12,27). With UPS Tapping (7) observed a rapid attenuation of the zirconium 5s and 4d conduction band levels and the appearance of a broad band at 5.6 eV below the Fermi level (E_F) upon the adsorption of 100 L of oxygen. This broad band is described as being associated with the oxygen 2p level. Using XPS, Sen et al. (12) observed the growth and shift of the oxygen 2p level to higher binding energy with increasing oxygen exposure. They found that at low exposures (40-70 L) the oxygen 2p band is centered near 5.9 eV but shifts to 7.0 eV following a large dose of 10^6 L. Also, employing XPS, Veal and coworkers (27) studied a fully oxidized zirconium surface and determined the following binding energies for the valence-band and near valence-band features: O 2p - 7.0 eV, O 2s - 22.5 eV and the Zr 4p band which shifts from 27.2 to 32.2 eV below E_F during oxidation. The zirconium 4p doublet was not resolved.

The oxidation state of zirconium as a function of oxygen exposure and depth is not well understood currently. Although several bulk oxides of zirconium have been observed (29), Veal et al. (27) suggest that only a dioxide surface species is present. Using XPS and static secondary ion mass spectrometry (SSIMS), Valyukhov et al. (9) also conclude that only the dioxide species is present during all stages of oxidation. They propose that the chemisorption of oxygen initially causes the formation of crystallization centers and that ZrO_2 islands form with increasing O_2 adsorption. These islands then grow until completion of a monolayer. Oxidation continues by

the diffusion of oxygen through the oxide layer to the metal-oxide interface. Two recent AES studies (10,11) agree with this mechanism for zirconium oxidation. However, Sen et al. (12) using XPS and AES propose that for low O_2 exposures (< 10 L) at room temperature, dissociative chemisorption leads to the formation of various suboxides. Using curve resolution of XPS data, they deduced that the suboxide species are converted into a single suboxide, probably ZrO , at larger O_2 exposures (10-25 L). Increasing oxygen exposure then causes some of the surface ZrO to be converted into ZrO_2 followed by the formation of a subsurface ZrO_2 layer through cation transport to the surface region. A submonolayer of surface ZrO is believed to remain, however, even after large doses. In order to substantiate their interpretation of the XPS results Sen et al. (12) monitored the zirconium $M_{4,5}VV$ Auger transition of the oxygen-exposed surface. Since ZrO_2 is a maximal valency ionic material (30), it is suggested that an interatomic Auger transition may be observable whereas for a submaximal valency oxide such as ZrO , no interatomic transition would be expected (31). In addition to the parent metal transition, two additional $M_{4,5}VV$ features were found to form and grow with oxygen exposure, one at 167 eV attributed to an interatomic transition associated with ZrO_2 and a second at 182 eV attributed to an intratomic zirconium transition possibly from a suboxide. These Auger results are similar to those obtained in a related study by Rao and Sarma (32) on the oxides of Ti, V and Mn. In order to confirm the presence of a suboxide surface species, Sen et al. (12) argon-ion sputtered the surface. During this process the 182 eV signal

decreased while the 167 eV signal did not change thereby suggesting that ZrO_2 lies beneath a mixture of ZrO_2 and a suboxide.

ELS is a technique which is sensitive to changes in both the occupied and unoccupied density of states (33-35). The technique is performed in either the transmission or reflection mode. In the transmission mode high energy electrons (> 10 KeV) impinge on a thin sample and electrons which are inelastically scattered while passing through the sample are energy analyzed. In the reflection mode electrons with energies in the range of 10 - 2000 eV impinge on the sample, and those which are backscattered are energy analyzed. Also, by employing reflection ELS and varying the primary beam energy, depth sensitive chemical information can be obtained (34,36). Therefore, reflection ELS should provide a useful means of characterizing the oxidation of a zirconium surface.

Very little ELS data exist for either the clean or oxygen-exposed zirconium surface. Frandon et al. (14) have presented transmission ELS data of zirconium metal and oxide. Reflection ELS spectra for zirconium and ZrN_x using a primary beam energy of 500 eV have been published by Schubert et al. (15). Also, using reflection ELS, Solomon and Grant (16) investigated the $M_{4,5}$ loss feature for the metal and oxide. Axellson et al. (11) have presented reflection ELS spectra of zirconium as a function of oxygen exposure but offer little interpretation of the data. It appears that no ELS investigations of zirconium metal or oxide have been published in which the primary beam energy has been varied. In the present study ELS results for zirconium metal and partially oxidized zirconium are

presented for primary beam energies ranging from 100 to 600 eV and a detailed interpretation of these results is offered. Clear evidence for the presence of suboxide formation is found and variations in the zirconium oxidation state with depth are observed.

ELS Background

Low energy ELS is a relatively easy experiment to perform, but the interpretation of the structure in ELS spectra is challenging and in most cases the loss structure is not well understood. Attempts at interpreting low energy ELS spectra generally utilize one of three models: a dielectric model (37-39), a density-of-states model (33,34,40,41), or a joint density-of-states model modified by exchange interactions (35).

The dielectric model is most appropriately applied to transmission ELS and to reflection ELS in the case of large primary beam energies ($E_p = 10^3 - 10^5$ eV). Under these conditions the losses which occur with appreciable probability are associated with collective excitations and single particle excitations which produce a small momentum change (compared to a reciprocal lattice vector) of the scattering electron. The interpretation of high-energy ELS spectra in terms of the dielectric model has proven very effective for nearly all substances ranging from wide-gap insulators such as the alkali halides to the nearly free-electron materials (39). However, the use of the dielectric model for low-energy ELS ($E_p < 500$ eV) may not be appropriate in many cases because the basic assumption of zero or small momentum change of the scattering electron is

invalid. This can be shown using the conservation laws. The conservation of momentum

$$\underline{K}_f - \underline{K}_i = \underline{\Delta K} = \underline{\Delta k} + \underline{G} \quad (2-1)$$

and the conservation of energy

$$\Delta E = \frac{\hbar^2}{8\pi^2 m_e} (|\underline{K}_i|^2 - |\underline{K}_f|^2) \quad (2-2)$$

lead to an expression for the range of momentum transfer to the scattering electron for a single inelastic collision.

$$\begin{aligned} \frac{8\pi^2 m_e \Delta E}{\hbar^2} &\geq |\underline{\Delta K}|^2 \geq |\underline{K}_i|^2 + |\underline{K}_f|^2 - 2|\underline{K}_i||\underline{K}_f| \\ &= \frac{8\pi^2 m_e}{\hbar^2} (E_o^{1/2} - (E_o - \Delta E)^{1/2})^2 \end{aligned} \quad (2-3)$$

Here the contribution of phonon modes has been neglected, ΔE is the energy loss of the primary electron, E_o is the primary electron energy, $\underline{K}_i$ and $\underline{K}_f$ are the initial and final wave vectors of the primary electron, $\underline{\Delta K}$ is the scattering vector or the momentum change of the primary electron, $\underline{\Delta k}$ is the total change in crystal momentum, and $\underline{G}$ is a reciprocal lattice vector. From equation (2-3) it is clear that for low-energy ELS (reflection unless otherwise stated) the dielectric model, which assumes $\underline{K} = \underline{0}$, is inappropriate. For example, a 100 eV electron which experiences a 10 eV loss in energy has a momentum change which lies between 21% and 133% of a reciprocal

lattice vector for ZrO_2 . However, it is expected that for $E_p > 100$ eV losses are associated with momenta changes near the minimum value. This results from the fact that the inelastic losses for $E_p > 100$ eV are primarily due to a screened Coulomb interaction which has a wave vector representation, in the Thomas-Fermi sense, proportional to $1/(k_0^2 + q^2)$ i.e. $V(q) \propto 1/(k_0^2 + q^2) = 1/(\underline{k}_0^2 + \underline{\Delta k}^2)$ where $V(\underline{q})$ is the wave vector representation of the Coulomb potential and $\underline{k}_0$ is the Thomas-Fermi wave vector. Thus, the interaction potential is inversely proportional to the square of the momentum transfer.

In inelastic electron scattering using a very low primary beam energy ($E_p < 100$ eV), exchange interactions, which arise as a consequence of the Pauli principle, as well as a Coulomb interaction must be taken into account (35). In addition to the influence of exchange forces and a finite momentum transfer in low-energy ELS, diffraction effects must also be considered for surfaces in which the grain size is large compared to the excitation volume. For such surfaces the spectra obtained are proportional to both the elastic and inelastic wave fields in the material (35,40,42). Bauer (35) has developed a model for the inelastic scattering of slow electrons. It incorporates the above considerations and offers an approximate expression for the measured intensity of inelastically scattered electrons which undergo indirect transitions as a function of energy.

$$I(\Delta E) = \sum_{c,v} \sum_{\underline{\Delta k}} L_{c,v}(\underline{k}, \underline{\Delta k}) \frac{d^2 \underline{k}}{|\bar{V}_{\underline{k}}(E_c(\underline{k} + \underline{\Delta k}) - E_v(\underline{k}))|_{E_c - E_v = \Delta E}} \quad (2-4)$$

The integral in equation (2-4) is a generalization of the joint density-of-states function used in the interpretation of optical data which accounts for finite momentum changes. The term $L_{c,v}(\underline{k}, \underline{\Delta k})$ can be considered to be a transition probability containing the momentum matrix element. From this expression it is apparent that maxima in intensity occur for $\underline{k}, \underline{\Delta k}$ pairs where the initial and final state energy bands are parallel.

Equation (2-4) can be simplified to give a density-of-states interpretation of certain features in the low-energy ELS spectra as shown by Ludeke and Esaki (33,41). If the initial valence-band state is narrow and the interband transition is isolated in energy from other transitions, then equation (2-4) can be restated as

$$I(\Delta E) = \sum_c \bar{L}_{c,v} D_c(\Delta E) \quad (2-5)$$

where $\bar{L}_{c,v}$ is the transition probability averaged over all possible $\underline{\Delta k}$, and $D_c(\Delta E)$ is the density of states of the conduction band. Therefore, assuming no modulation in $\bar{L}_{c,v}$ due to partial filling of the conduction band from a competing transition arising from a different initial state, the low-energy ELS spectra should be proportional to the conduction band density of states.

To further assist in the interpretation of ELS features associated with interband transitions, the consequences of selection rules should be considered. For high primary beam energies, it is well known that interband transitions can be described in terms of optically allowed or dipole-allowed transitions (43). The dipole-

selection rule is $\Delta J = 0, \pm 1$ and arises directly from the first Born approximation. Here ΔJ is the change in the total angular momentum of the system. The validity of the first Born approximation is, however, questionable at low primary beam energies because of the importance of exchange forces. Thus, at $E_p < 100$ eV a breakdown in the dipole-selection rule is expected and quadrupole-allowed transitions should increase in importance. This fact has been utilized by Ludeke and Koma (43) and Colavita et al. (44) to identify loss features as quadrupole-allowed transitions which are dipole forbidden for the materials which they studied.

Experimental Procedure

A polycrystalline zirconium foil of 99.99% purity and approximate dimensions of 15 x 10 x 0.12 mm was used in this study. The sample was etched in a hydrofluoric acid solution in order to remove most of the accumulated oxide layer. The sample was then solvent cleaned in ethanol and spot welded onto two tungsten support wires. A tungsten filament was used to heat the sample radiantly up to about 1400 K. Temperatures above this were attained using electron bombardment.

In order to obtain a clean surface the sample was argon-ion sputtered and annealed in vacuum at 1500 K repeatedly. An Auger spectrum of the annealed surface is shown in figure 2-1. The sample was heated briefly to 1000 K and allowed to cool prior to taking each ELS spectrum of the clean metal in order to remove any small amount of contamination which may have accumulated during the previous

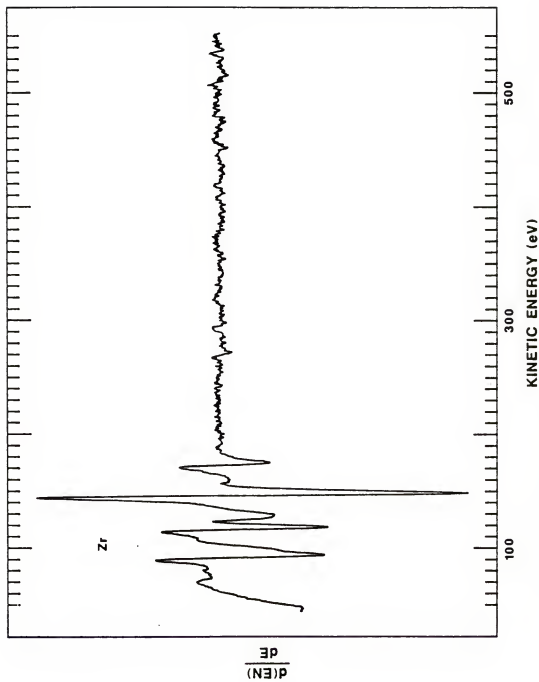


Figure 2-1. AES spectrum taken from a polycrystalline zirconium surface cleaned by repeated sputtering and annealing at 1500 K.

run. The oxidized surface was formed using a 40 L, room-temperature dose of oxygen. This lies within the 10-60 L range that results in a maximum amount of suboxide formation according to Sen et al. (12). An AES spectrum of the partially oxidized sample is shown in figure 2-2.

This study was performed in an ultrahigh vacuum system (base pressure of 2×10^{-10} Torr) which has been described previously (45). AES and ELS spectra were collected using a PHI double-pass cylindrical mirror analyzer (CMA) with the sample mounted at an angle of 45° with respect to the coaxial electron gun. ELS was performed in the retarding mode using pulse counting (46) and a pass energy of 25 eV ($\Delta E/E_{\text{pass}} = 0.016$). Ten 2000 channel spectra were taken with a maximum count per channel of 8000. The summation of these spectra was then averaged with a spline quadratic fit to achieve the presented spectra. A primary beam current of 100 nA over a spot size of approximately 0.1 mm was used. The full width at half maximum (FWHM) of the primary beam decreased from 0.82 eV at $E_p = 600$ eV to 0.52 eV at $E_p = 100$ eV. A very high S/N ratio was obtained in these ELS experiments. Although many features appear to be small in the figures presented, expanded-scale figures used in the data analysis show that these features are real and have intensities much larger than background noise.

AES was performed in the nonretarding mode using a primary electron beam energy of 3 keV. Lock-in detection was used with a 0.5 volt peak-to-peak (V_{pp}) sine wave of 10 kHz applied to the outer cylinder of the CMA.

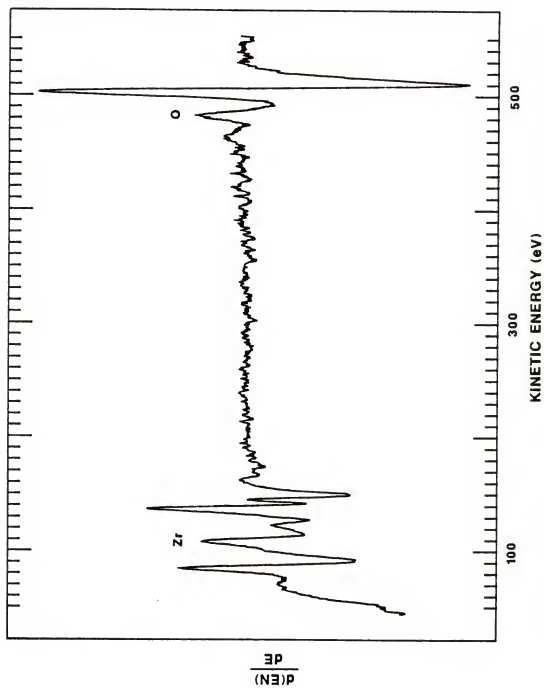


Figure 2-2. AES spectrum taken after an exposure to 40 L of oxygen at 300 K.

ELS Results and Discussion

Clean Polycrystalline Zirconium

ELS spectra taken from a clean polycrystalline zirconium sample are shown in figure 2-3. Five spectra are presented which were obtained with primary beam energies of 100, 150, 300, 400 and 600 eV. Since the depth sensitivity of ELS varies with primary beam energy, this figure is essentially a depth profile of the surface region of zirconium. On the bases of inelastic mean free path data, it is estimated that the sampling depth for the various primary beam energies used is 100 eV - 3.5 atomic layers, 150 eV - 4 atomic layers, 300 eV - 5.8 atomic layers, 400 eV - 6.6 atomic layers and 600 eV - 8 atomic layers. In Table 2-1 many of the loss features shown in figure 2-3 are designated according to the loss mechanism believed to be responsible, i.e. either an electronic transition or a collective mode excitation (plasma oscillation).

Plasmon excitations

It is well known that bulk plasmon features become less prominent while surface plasmon features become more prominent as the technique becomes more surface sensitive (39). In ELS the surface sensitivity is enhanced either by using smaller primary beam energies or by using grazing incidence and detection angles. This behavior of plasmons can be useful both in identifying features as plasmons and in distinguishing between a bulk or a surface plasmon. However, the fact that a peak becomes more or less prominent as the surface

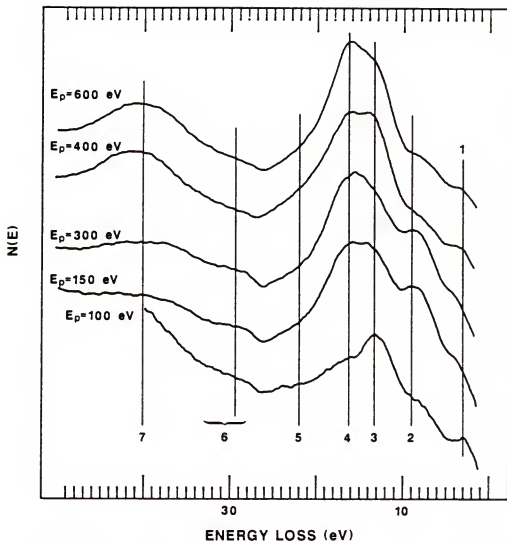


Figure 2-3. ELS spectra taken from the zirconium surface shown in figure 2-1 using primary beam energies of 100, 150, 300, 400 and 600 eV. Loss features are designated according to the mechanisms believed to be responsible. The peak assignments are summarized in Table 2-1 and in the text.

Table 2-1. Clean Zirconium ELS Assignments

<u>Feature</u>	<u>Assignment</u>	<u>Loss Energy (eV)</u>
1	Zr 4d - Zr 4d	3.0
2	Zr 4d - Zr 5p	9.0
3	surface plasmon	13.1
4	bulk plasmon	16.3
5	Zr 4d - Zr 4f	22.
6	Zr 4p - Zr 4d	28.0 - 33.0
7	Zr 4p - Zr $4p^{-1}_{4,\epsilon d}$	40.

sensitivity varies does not always imply that it is a plasmon particularly when the homogeneity of the sample varies with depth.

The peak at 16.3 eV is seen to decrease relative to adjacent features with decreasing primary beam energy. This feature is also observed to decrease much more rapidly than adjacent features upon the adsorption of small amounts of oxygen or hydrogen (11,47). This behavior is characteristic of bulk plasmon loss features in the near surface region, and thus, the 16.3 eV feature is assigned as such. This assignment is consistent with the optical data of Lynch et al. (13), the transmission ELS results of Frandon et al. (14) and the ELS results of Schubert et al. (15). A surface plasmon excitation associated with the bulk plasmon excitation is assigned to the loss features at 13.2 eV. This feature is most easily seen in the spectra where $E_p = 100$ eV and is observed to decrease relative to adjacent features with increasing E_p . The deviation of the bulk and surface plasmon frequencies from their free electron values of $W_p = (4\pi ne^2/m_e)^{1/2}$ (n = valence electron concentration) and $W_s = W_p/\sqrt{2}$ is due to the departure of the dielectric function from that of a free electron gas. This is caused by the addition of the crystal lattice and the appearance of single particle excitations (39). It is evident from figure 2-3 that due to the presence of interband transitions in the same loss energy region, the peak shapes and precise energies of the plasmon losses are difficult to determine. However, there seems to be reasonable evidence for their identification as plasmon losses.

Electronic transitions

The shoulder beginning at about 3 eV is assigned as an intraband transition from filled regions of the Zr 4d band to empty regions of the Zr 4d band based on the optical conductivity data of Lynch et al. (13). In optical conductivity data peaks are associated with dipole-allowed electronic transitions (44). A broad peak in the zirconium conductivity data from 1 to 3 eV is observed and, based on the band structure calculations of Jepsen et al. (48), can be assigned as transitions between parallel flat bands along the region from T' to E and at P and K in the first Brillouin zone as depicted by Jepsen et al. (48). However, due to the indirect nature of electronic transitions associated with low energy ELS, the assignment of the 4 eV shoulder to particular symmetry points can only be made tentatively. Jepsen et al. (48) also suggest that the 4d band of zirconium is hybridized with some s and p character so a particular selection rule is difficult to apply with regard to describing this transition.

A simplified energy level diagram is presented in figure 2-4 which shows the occupied and unoccupied energy levels of zirconium near the Fermi level. The remaining ELS features which have not been discussed are all assigned as interband transitions and are depicted in figure 2-4. The occupied levels are determined from XPS results obtained in this laboratory, XPS results from Veal et al. (27) and XPS and UPS results from Tapping (7). The unoccupied levels are assigned so as to be consistent with the ELS results presented here, the density of states as calculated by Jepsen et al. (48) and the

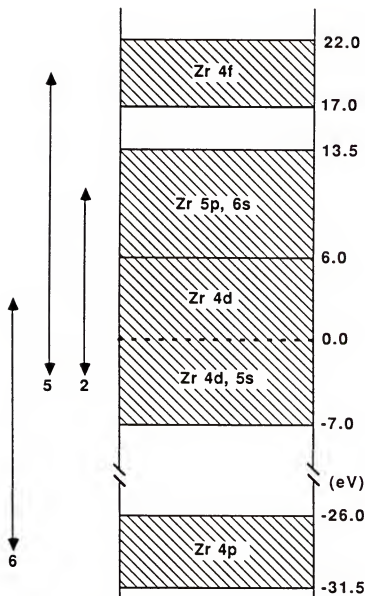


Figure 2-4. Occupied and unoccupied energy levels of zirconium obtained from the ELS spectra and other sources (see text). The electronic transitions larger than 4 eV are depicted, and the transitions are labelled as in figure 2-3.

bremsstrahlung data presented by Speier et al. (28). For the low-energy features, the angular momentum character of the unoccupied levels is determined from a partial-wave analysis of the calculated density of states from Speier et al. (28). The characters of the higher-energy levels are deduced from the Zr 4p and 4d initial state transitions from the present ELS data and are based on dipole-allowed transitions only.

The interband transitions shown in figure 2-4 are assigned to the loss features as follows. The shoulder at about 8.5 eV can be attributed to transitions from the Zr 4d and 5s conduction band levels to the unoccupied Zr 5p level. The shoulder beginning at 19 eV and extending to 26 eV can be tentatively assigned to a Zr 4d-to-Zr 4f interband transition. The remaining identified interband transitions which lie above 26 eV in the energy loss spectra are due to the excitation of the Zr 4p core level. The loss features with energies in the range from 28 eV to 33 eV are assigned as transitions from the Zr 4p level to the empty Zr 4d levels just above E_F . The broad peak centered near 40 eV is due to an excitation of the Zr 4p level to a level 11 eV above E_F which can be associated with high lying terms in the atomic $4p^{-1}4d^{n+1}$ multiplet. This state is designated $4p^{-1}\overline{4,cd}$ and has been well documented for transition metals with less than half-filled conduction band d levels (49-51).

Oxygen-exposed Zirconium

The interpretation of the oxygen-exposed zirconium ELS spectra is difficult due to the fact that density-of-states calculations are

not available for monoclinic ZrO_2 . Monoclinic ZrO_2 is the only polymorph of zirconia which is stable below 1300 K in its pure state. Discrete-variational-X α cluster calculations have been performed for the tetragonal and cubic phases of zirconia (30). However, these calculations only reveal states in the first 3 eV of the conduction band. These states are mostly Zr 4d in character near E_f with some O 2p character which increases in importance with increasing energy.

ELS spectra for oxygen-exposed zirconium are presented in figures 2-5 and 2-6. Spectra are shown for primary beam energies of 100, 200, 400 and 600 eV, and many of the loss features are denoted according to the loss mechanism believed to be responsible in Table 2-2.

Plasmon excitations

The peak at 26 eV is assigned as a bulk plasmon in agreement with Frandon et al. (14). This assignment is supported by three points. Firstly, the intensity of this feature increases as E_p increases which is characteristic of a bulk plasmon. Secondly, the loss energy is near the calculated plasmon energy of 22.0 eV for ZrO_2 which is expected based on a simple dielectric model for bound electrons (39). Thirdly, an ELS feature near 23 eV from polycrystalline titania, which has an electronic structure similar to that of zirconia, has been assigned as a bulk plasmon (52).

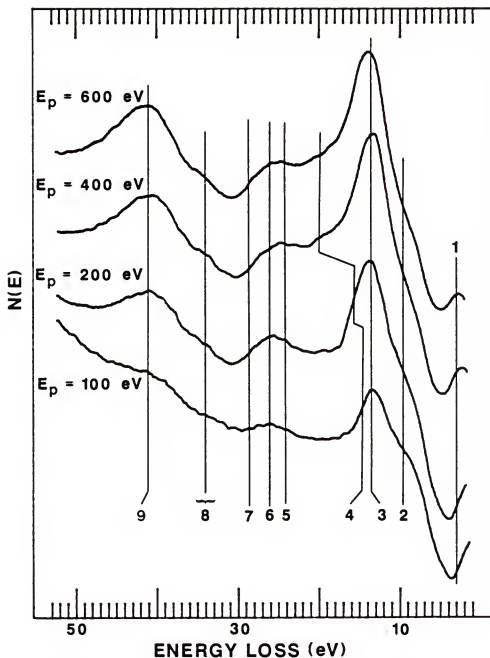


Figure 2-5. ELS spectra taken from the oxygen-exposed zirconium surface shown in figure 2-2 using primary beam energies of 100, 200, 400 and 600 eV. Loss features are designated according to the loss mechanisms believed to be responsible. The peak assignments are summarized in Table 2-2 and in the text.

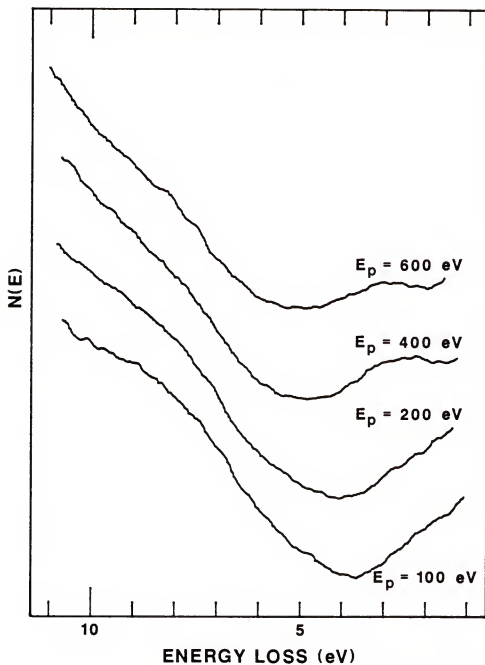


Figure 2-6. Enlargement of low energy-loss region of the ELS spectra shown in figure 2-5.

Table 2-2. Partially Oxidized Zirconium ELS Assignments

<u>Feature</u>	<u>Assignments</u>	<u>Energy Peak</u>
1	Zr 4d - Zr 4d	3.
2	O 2p - Zr 5s	9.5
3	O 2p - O 3s	13.5
4	O 2p - Zr 6s	20.0
5	O 2s - O 2p antibond.	24.
6	bulk plasmon	26.0
7	O 2s - Zr 5p	29.
8	Zr 4p - Zr 4d	33.0-36.5
9	Zr 4p - Zr 4p ⁻¹ _{4,εd}	41.0

Electronic transitions

The low-energy loss feature in the 1 to 3 eV region, which is best seen in figure 2-6, is attributed to transitions from filled to empty states in the Zr 4d band. It is believed to be due to the presence of zirconium in an oxidation state lower than +4. A similar feature is also observed in loss spectra of titanium oxides (53-55) and is highly sensitive to the oxidation state of the titanium and the geometrical structure of the surface. Titanium as Ti^{3+} has transitions with energy losses greater than 2 eV, and Ti^{2+} has electronic transitions responsible for loss features in the energy range from 1 to 3 eV (53,56). Applying these titanium results to the analogous zirconium system and based on figures 2-5 and 2-6, mean free path data, and following a 40-L oxygen dose, the surface region has ZrO -like states in the first 5 atomic layers and Zr_2O_3 -like states in the next five to eight atomic layers. However, the oxidation state of the zirconium appears to change continuously. This is most easily seen by the steady shift in the band gap from 4.9 eV at $E_p = 100$ eV to 6.1 eV at $E_p = 600$ eV. Here the band gap is estimated by drawing a linear extension of the low-energy portion of the 9 eV shoulder to the baseline.

The electronic nature of the low-energy loss feature can be viewed in various ways (53,54,56). A purely ionic model can be considered in which Zr^{3+} has one valence d electron and Zr^{2+} has two valence d electrons. Thus, a greater number of allowed transitions would be expected for Zr^{2+} than for Zr^{3+} . A ligand-field model can also be considered. Here the interactions of the zirconium valence

electrons with the oxygen ligand would cause the splitting of the valence energy levels and energy-loss features could arise from allowed transitions between these split levels. The $4d^2$ configuration of Zr^{2+} would have a more complicated splitting of levels, and thus, more allowed transitions would be possible than for the $4d^1$ configuration of Zr^{3+} . An additional explanation may be reduced cation screening in lower oxidation states (54). The oxygen anions can be considered to screen the zirconium cations in ZrO_2 . However, for lower oxidation states the cations are not completely screened. These partially screened cations may then share valence d electrons creating bonding and antibonding levels for these electrons between which allowed transitions may occur. Again, two shared electrons would have a more complicated orbital structure giving rise to more allowed transitions than one shared electron.

Figure 2-7 shows a simplified energy-level diagram for ZrO_2 . The energy levels below the Fermi level are assigned in accordance with XPS data taken in this laboratory, the XPS data of Veal et al. (27) and the UPS results of Tapping (7). The energy levels above the Fermi level are assigned so as to be consistent with the calculations of Morinaga et al. (30), the transmission ELS data of Frandon et al. (14), the core level ELS data of Solomon and Grant (16) and the ELS data presented in this study. The electronic transitions resulting in loss features above 3 eV are also depicted in figure 2-7 and are related to the features in the ELS spectra as described below.

Loss features associated with the $0\ 2p$ initial state are possibly the shoulder at about 9.5 eV, the 13.5 eV peak and the broad

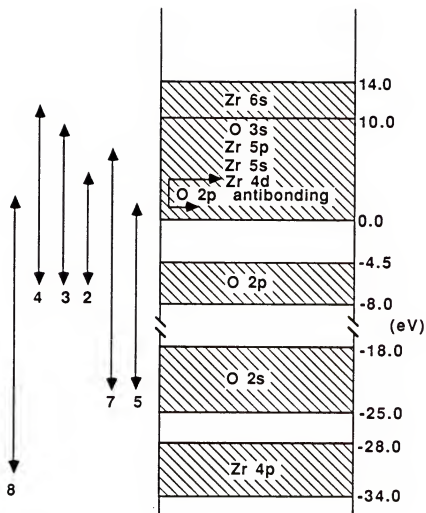


Figure 2-7. Occupied and unoccupied energy levels of zirconium dioxide obtained from ELS spectra and other sources (see text). The electronic transitions larger than 3 eV are depicted, and the transitions are labelled as in figure 2-5.

shoulder in the 400 and 600 eV spectra near 20 eV. Based on the derived energy level diagram, the 9.5 eV shoulder can be assigned to transitions to the Zr 5s unoccupied level. This is in contrast to the assignment of Frandon et al. (14) who suggested that the final state is the empty Zr 4d levels. The predominant peak in the loss spectra at 13.5 eV can be attributed to a transition between the oxygen 2p and 3s levels. Axellson et al. (11) and Frandon et al. (14) have assigned this peak as a bulk plasmon loss. However, the energy position of this loss feature does not agree with the calculated bulk plasmon energy. Also, the loss energy of this feature does not change with varying zirconium oxidation state (i.e. the loss energy is not a function of E_p) as would be expected of a plasmon loss due to the changing valence band electron concentration. Thus, an interband transition seems to be a more plausible assignment for the 13.5 eV loss peak.

The broad shoulder in the 400 and 600 eV spectra at about 20 eV can be assigned as a transition from the oxygen 2p level to the Zr 6s level. The absence of this feature in the 100 and 200 eV spectra is believed to be due to the change in the oxidation state of the zirconium with depth. This change may cause the Zr 6s level and/or the O 2p level to move toward the Fermi level resulting in a shift of the loss feature associated with a transition between these energy levels to beneath the 13.5 eV peak. A shift to lower binding energy of the O 2p band with a decreasing oxidation state is consistent with the XPS results of Sen et al. (12).

Two dipole transitions can be expected to arise from the $0\ 2s$ level. The final states of these transitions would be the $0\ 2p$ antibonding level and the $Zr\ 5p$ level. The loss peaks associated with these transitions should occur near 24 and 29 eV and may lie beneath the 26 eV plasmon peak. These loss features, however, can be seen clearly in the transmission ELS spectra of Frandon et al. (14). The inability to resolve these transitions here may be due to the partial oxidation of the sample which may result in weak $0\ 2s$ transitions. Frandon et al. had oxidized their sample to a greater extent by exposing it to the atmosphere.

The remaining loss features arise from the excitation of the $Zr\ 4p$ level. Several small features between 33.0 and 36.5 eV can be assigned as transitions to the unoccupied $Zr\ 4d$ levels just above E_F . The large loss feature at 41.0 eV can be assigned, as in the clean metal, as a transition to an energy level about 11 eV above E_F associated with high lying terms in the $4p^{-1}4d^{n+1}$ multiplet. It is interesting to note a sharpening of this peak compared to that of the clean metal and a rapid attenuation of it with decreasing primary beam energy. This is observed not only for oxygen-exposed zirconium but also for hydrogen-exposed zirconium (47). The reasons for this behavior are not understood.

Conclusions

Electron energy loss spectra for clean and oxygen-exposed polycrystalline zirconium have been interpreted in terms of a density-of-states model. All major loss features have been

identified as either collective mode excitations (plasma oscillations) or electronic transitions. Based on this interpretation the angular momentum character and the binding energies of the unoccupied levels of clean and partially oxidized zirconium have been determined. The energies of the lower unoccupied levels of clean zirconium characterized here using ELS agree well with those determined using bremsstrahlung spectroscopy (28), and the energies and angular momenta of the levels agree with those obtained using calculational methods (28,48). The higher lying unoccupied levels of clean zirconium and all but the lowest unoccupied levels of oxygen-exposed zirconium characterized here using ELS have not been presented in the literature previously.

The oxidation state of a zirconium surface following a saturation dose of oxygen is found to increase with depth. Evidence for ZrO -like states in the first five atomic layers is observed. In approximately the next five to eight layers, Zr_2O_3 -like states are observed. The oxidation state appears to vary continuously with depth suggesting the presence of non-stoichiometric oxides.

CHAPTER III
AN INTERPRETATION OF ELS SPECTRA FROM POLYCRYSTALLINE
ZIRCONIUM SURFACES AFTER EXPOSURE TO H_2 AND H_2/O_2

Introduction

The adsorption of hydrogen on a clean zirconium surface has been studied using ultraviolet photoemission spectroscopy (UPS) (7,27,57,58), temperature programmed desorption (TPD) (8,59) and nuclear magnetic resonance (NMR) (60). Lin and Gilbert (59) determined a maximum sticking coefficient of 6.5×10^{-4} at 770 K, and Foord et al. (8) claim that deuterium is efficiently absorbed beneath the surface even at 300 K. However, these studies offer no information about the depth of the hydrided layer, the distribution of hydrogen in this layer or the adsorption kinetics. This lack of fundamental information about hydrogen adsorption on a zirconium surface is primarily due to the difficulty of detecting hydrogen in the surface region of a material using most surface characterization techniques.

Detecting hydrogen is difficult because hydrogen has no core level electrons and, therefore, gives no distinct core-level photoemission or Auger features. Hydrogen is also difficult to detect using vibrational spectroscopies because it has a low mass which results in low vibrational mode intensities. Moreover, vibrational spectroscopies do not readily allow for the detection of hydrogen beneath the surface layer. Furthermore, hydrogen generally induces only small changes in the occupied valence-band density-of-

states of the substrate in the surface region. However, small variations in the occupied density of states combined with associated changes in the unoccupied density of states can result in large variations in the joint density of states near the Fermi level. Therefore, electron energy loss spectroscopy (ELS) is well suited for the detection of hydrogen since many ELS features are due to intraband or interband transitions which are a function of the joint density of states near the Fermi level. In addition to intraband and interband transitions, ELS features due to surface and bulk plasma oscillations are often present. Surface plasma oscillations are particularly sensitive to changes in the energy and spacial distributions of electrons near the Fermi level in the near-surface region. Both of these types of changes are induced upon hydrogen adsorption. Consequently, ELS has been used successfully for the detection of hydrogen in the surface region of metals, semiconductors, and insulators (61-64).

In addition to the detection of hydrogen, the hydrogen distribution in the surface region of a material may be determined by depth profiling using ELS. ELS depth profiles can be obtained by varying the primary beam energy or by varying the incident and/or detected angle. Depth profiling with ELS has been used to study the oxidation of zirconium (65) and tin (66) and the reduction of tin oxide (34). These studies demonstrate that ELS is often sensitive to electronic or chemical state changes which are difficult to detect using either X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES). Furthermore, ELS may be used to examine hydrogen

diffusion to or away from the surface as a function of temperature. From this it may be possible to obtain activation energies for diffusion and diffusion coefficients.

This study is part of an ongoing effort to understand the O/Zr, H/Zr and H/O/Zr systems (1-4,65). ELS spectra are presented for hydrogen-exposed zirconium and oxygen- and hydrogen-exposed zirconium. The primary beam energy was varied to obtain depth profiles of the surface region. These data and their interpretation form a basis for further detailed studies of the hydrogen-zirconium interaction.

Experimental Procedure

A polycrystalline zirconium foil (15 x 10 x 0.12 mm) of 99.99% purity was used in this study. The sample was etched in a hydrofluoric acid solution in order to remove most of the accumulated oxide layer. The sample was then solvent cleaned in ethanol and spot welded onto two 0.020 in. tungsten support wires. A tungsten filament was used to heat the sample radiantly up to about 1400 K. Temperatures above this were attained using electron bombardment. The sample temperature was monitored using an optical pyrometer.

In order to obtain a clean surface, the sample was annealed in vacuum at 1500 K for 1 hour followed by repeated argon ion sputtering and annealing at 850 K. AES and ion scattering spectroscopy (ISS) were used to monitor the surface cleanliness particularly with regard to possible sulfur and chlorine contamination (3). An AES spectrum of the clean, annealed surface is shown in figure 2-1. The hydrided

surface was formed using a 2000 L dose of hydrogen at 770 K. The hydrogen-exposed/oxygen-exposed surface was formed by exposure to 2000 L of hydrogen at 770 K followed by a 40 L dose of oxygen at room temperature.

This study was performed in an ultrahigh vacuum system (base pressure of 2×10^{-10} Torr) which has been described previously (45). ELS and AES spectra were collected using a PHI double-pass cylindrical mirror analyzer (CMA) with the sample mounted at an angle of 45° with respect to the coaxial electron gun. ELS was performed in the retarding mode using pulse counting (46) and a pass energy of 25 eV ($\Delta E/E_{\text{pass}} = 0.016$). Ten, 2000-channel spectra over a 100 V range were taken with a maximum count rate of 8,000 counts/channel. The summation of these spectra was then averaged with a spline quadratic fit to obtain the ELS spectra. A primary beam current of 100 nA over a spot size of approximately 0.1 mm was used. The full width at half maximum (FWHM) of the elastic peak decreased from 0.82 eV at a primary beam energy (E_p) of 600 eV to 0.52 eV at $E_p = 100$ eV. A very high signal-to-noise ratio was obtained in these ELS experiments. Although many features appear to be small in the figures presented, expanded-scale figures used in the data analysis show that these features are real and reproducible with intensities much larger than background noise. AES was performed using a primary electron beam energy of 3 keV and by operating the analyzer in the nonretarding mode. Lock-in detection was used with a $0.5 V_{pp}$, 10 kHz sine wave applied to the outer cylinder of the CMA.

Results and Discussion

Although low energy ELS is a technique that is very sensitive to adsorbate-induced changes in the surface region of a material, the interpretation of the spectra is difficult. Attempts at interpreting ELS spectra generally utilize one of three models: a dielectric model (37-39), a density-of-states model (33,34,40,41,65), or a joint density-of-states model modified by exchange interactions (35). A summary of these models has been presented recently (65) so they will not be discussed further here. The interpretation of the ELS spectra given below assumes dipole-allowed transitions only and is based on the density-of-states model.

Hydrogen-exposed Zirconium

The sensitivity of low energy ELS for the detection of hydrogen is demonstrated by comparing the energy loss spectra shown in figures 2-3 and 3-1. ELS spectra taken from a clean zirconium surface are shown in figure 2-3, and spectra from a hydrogen-exposed zirconium surface are shown in figure 3-1. In both figures spectra are presented that were obtained using primary beam energies of 100, 150, 200, 400 and 600 eV. It is clear from the differences between the spectra in these figures that ELS is sensitive to the presence of hydrogen in the surface region of zirconium.

The loss features of the hydrogen-exposed zirconium are difficult to assign because the chemical state of the zirconium is not known and may not even be well defined. However, based on previous studies (7,27,57) it is reasonable to assume that the

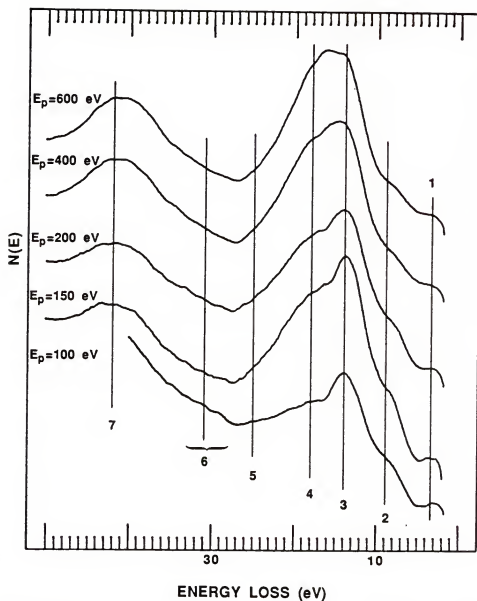


Figure 3-1. ELS spectra taken from the clean surface following a dose of 2000 L of hydrogen at 770 K using primary beam energies of 100, 150, 200, 400 and 600 eV. Loss features are designated according to the mechanism believed to be responsible and are given in Table 3-2.

chemical state is ZrH_x where $1 < x < 1.7$. This allows interpretation of the ELS spectra based on the UPS results (7,27,57,58) and band structure calculations of zirconium hydrides (67-70). The occupied density-of-states determined in these studies are summarized in Table 3-1, and the unoccupied levels are determined so as to be consistent with the band-structure calculations and the ELS spectra presented in this study.

Assignments of the loss features in the ELS spectra from the hydrogen-exposed zirconium are given in Table 3-2. The low energy loss feature near 3.5 eV can be attributed to an intraband transition within the Zr 4d band. This assignment is based on the optical absorption spectra calculated from the joint density-of-states by Gupta and Chatterjee (67). Features in optical absorption spectra result from direct electronic transitions whereas features in ELS spectra are due only to indirect electronic transitions. This creates problems in comparing optical absorption spectra and ELS spectra. However, the transitions responsible for the 3.5 eV loss feature have a change in wave vector which is about 5% of a reciprocal lattice vector (65). Therefore, an assignment of the 3.5 eV ELS loss feature based on optical spectra is reasonable.

All of the other loss features can be described as interband transitions. The small shoulder near 9 eV loss energy is assigned as a transition from the Zr 4d valence-band level to the Zr 5p conduction band about 9 eV above E_F . It is proposed that the dominant loss feature at 14.0 eV is due to a transition from the bonding H 1s/Zr 5s level located 5 eV below E_F to the Zr 5p

Table 3-1. Occupied Energy Level Peak Positions
for Hydrogen-exposed Zirconium

<u>Level</u>	<u>Energy Peak below E_F (eV)</u>
Zr 4d	1.
H 1s - Zr 5s	5.
Hydrogen antibonding	7.
Zr 4p	28., 29.5

Table 3-2. Hydrogen-exposed Zirconium ELS Assignments

<u>Feature</u>	<u>Assignment</u>	<u>Loss Energy (eV)</u>
1	Zr 4d - Zr 4d	3.5
2	Zr 4d - Zr 5p	9.
3,4	H 1s-Zr 5s - Zr 5p	14.0, 18.
5	Zr 4d - Zr 4f	25.
6	Zr 4p - Zr 4d	28.-33.
7	Zr 4p - Zr 4p ⁻¹ _{4,ed}	42.

conduction-band level. Plasmon loss features are relatively easy to identify because they vary strongly with sampling depth; that is a bulk plasmon loss feature increases in intensity with increasing probed depth whereas a surface plasmon loss feature decreases rapidly with increasing probed depth. Therefore, this particular loss feature is not believed to be associated with a plasmon excitation because no marked variation in this feature is observed with varying primary beam energy. The small attenuation of the 14.0 eV loss feature with increasing primary beam energy is believed to be due to a decrease in the hydride concentration with depth. The broad loss feature ranging from about 16 to 25 eV in loss energy is probably composed of at least two electronic transitions. The first may be a transition from the hydrogen antibonding level about 7 eV below E_f to the Zr 5p unoccupied level. A second may involve a transition from the Zr 4d level to an unoccupied level approximately 24 eV above E_f which would have 4f character under the assumption of dipole-allowed transitions.

The remaining loss features above 25 eV loss energy are associated with the excitation of the Zr 4p core levels. The broad shoulder ranging from about 28 to 33 eV loss energy is assigned as transitions from the Zr 4p levels to the unoccupied Zr 4d levels extending from 1 to 5 eV above E_f . The large peak near 42 eV loss energy is assigned as a transition of the Zr 4p level to a level approximately 12 eV above E_f which is associated with high lying terms in the atomic $4p^{-1}4d^{n+1}$ multiplet. This state is designated

$4p^{-1}4_{ed}$, ϵ_d and has been well documented for transition metals with less than half-filled, conduction-band d levels (49,51,52). The ϵ refers to the energy of this state above the Fermi level.

A close inspection of figures 2-3 and 3-1 reveals that although the spectra from the hydrogen-dosed surface are quite different from the spectra of the cleaned surface for primary beam energies of 150, 200, and 400 eV, the spectra are similar for primary beam energies of 100 and 600 eV. These similarities and differences in the spectra are more clearly shown in figure 3-2 where the dashed-line spectra were taken from the cleaned surface and the solid-line spectra were taken from the hydrogen-exposed surface. Figures 3-2(a) through (c) were obtained using primary beam energies of 600, 150 and 100 eV respectively. The intensities of the spectra for each primary beam energy are normalized to one another. The similarity in the 600 eV spectra is believed to be due to a reduced hydrogen concentration at the depth probed by the 600 eV beam. At this depth the hydrogen-exposed zirconium is primarily in a metallic state with only a small hydride concentration. This small hydride concentration is evident by the increase in the 18 to 25 eV shoulder, the increase in the intensity at 14 eV and the reduction in the 9 eV shoulder. Also, an increase in the intensity of the broad 41 eV peak can be observed in figure 3-2(a). This increase is observed in all the hydrogen-exposed ELS spectra and is also observed following exposure of a zirconium surface to oxygen and carbon monoxide. The reason for this increase is not well understood. Although the 600 eV primary beam allows for the surface region to be probed more deeply than lower primary beam

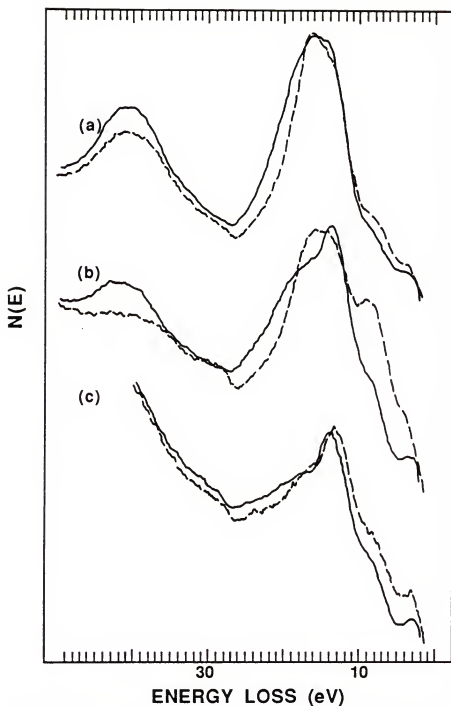


Figure 3-2. ELS spectra obtained using primary beam energies of (a) 600 eV, (b) 150 eV and (c) 100 eV. The dashed-line spectra are from the cleaned surface, and the solid-line spectra are from the hydrogen exposed surface.

energies, the near-surface region is also being probed. Therefore, the small hydride contribution in the 600 eV spectrum is at least partly due to the surface hydride. However, the large metallic contribution to the 600 eV hydrogen-exposed spectrum is due solely to a metallic state lying beneath the surface hydride. The variation in the hydrogen concentration with depth is discussed further below.

Although the 100 eV spectra shown in figure 3-2(c) appear to be similar, there are subtle but important differences indicative of the fact that they were taken from surfaces with different electronic structures. Differences upon hydrogen exposure include reductions in the 3.5 eV feature and the 9 eV shoulder, an increase in the 18 to 25 eV shoulder and an energy shift and primary beam energy dependence of the main loss peak. The variations in the 3.5 and 9 eV features are probably due to the reduction of the occupied density-of-states of the Zr 4d band following the adsorption of hydrogen (7,27,57,58). The increase in the relative intensity of the 18 to 25 eV shoulder in the hydrogen-exposed spectrum is most likely due to the appearance of the H-H antibonding level in the occupied density of states. The 0.9 eV energy shift of the main loss peak also supports the interpretation that these two spectra are from surfaces with different electronic structures because this shift cannot be explained by a work function change or charging effects in ELS. Also, the loss mechanisms of the main loss peaks are different for the cleaned and hydrided surfaces. Since the 13.1 eV loss peak of the cleaned surface decreases significantly with increasing primary beam energy (as seen by comparing figures 3-2(c) and 3-2(b), the 13.1

eV loss peak of the cleaned surface is assigned as a surface plasmon excitation (65). However, it is not likely that the 14.0 eV loss peak of the hydrogen-exposed surface is due to a surface plasmon excitation as discussed above.

It is apparent from figures 3-1 and 3-2 that the hydrogen concentration varies with primary beam energy. Evidence of a hydride is present in the 100, 150, 200 and 400 eV spectra whereas the 600 eV spectrum is more metallic like. By using the first-order term in the Poisson distribution and the inelastic mean free path data compiled by Seah and Dench (71), it is estimated that the depth sensitivities for the various primary beam energies for the hydrogen-exposed zirconium surface are 100 eV--6 atomic layers, 150 eV--7 atomic layers, 200 eV--8 atomic layers, 400 eV--11 atomic layers, and 600 eV--13.5 atomic layers. Based on the lattice constant used in the band structure calculations (67-70), the formulation proposed by Seah and Dench (71) and the fact that the 600 eV spectrum has a large metallic contribution, it appears that the depth of the hydride layer formed is approximately 30 to 40 Å thick for the exposure conditions used. Furthermore, it is estimated that an amount of hydrogen equivalent to approximately 7 monolayers has adsorbed and incorporated into about the first 11 layers of the zirconium surface. This suggests an overall sticking coefficient of about 3.5×10^{-3} which is somewhat greater than the sticking coefficient of 6.5×10^{-4} at 770 K determined by Lin and Gilbert (59). The discrepancy could be due to the fact that a filament was used to heat the sample in the present study which may have dissociated some of the hydrogen

allowing it to adsorb more efficiently. It is also possible that the surface studied by Lin and Gilbert was contaminated with S or Cl since the sample was only heated but not sputtered. In this case the sticking coefficient would be lower than that obtained from a clean surface which could also explain the discrepancy in measured sticking coefficients.

Hydrogen-exposed/Oxygen-exposed Zirconium

The hydrogen-exposed/oxygen-exposed ELS spectra are similar to spectra obtained from an oxygen-dosed zirconium surface (65). This similarity can be seen in figure 3-3 which shows a comparison between ELS spectra taken with primary beam energies of (A) 200 eV and (B) 600 eV from two room-temperature, 40 L oxygen-exposed surfaces. The dashed-line spectra were taken from a cleaned surface, and the solid-line spectra were taken from a 2000 L hydrogen-exposed surface. The intensities of the spectra for each primary beam energy are normalized to one another. Although the spectra taken from the cleaned and hydrogen-exposed surfaces are similar, there are small differences in the relative intensities of the loss features. Based on a previous TPD and energy-resolved ESD study of zirconium (1), the cause of the intensity variations may be due to the coexistence, in varying concentrations, of a hydride, an oxide and/or a hydroxylated-oxide surface region. It was determined from the ESD results obtained from a zirconium surface prepared using the same dosing conditions as in this study that hydrogen desorbs from both oxygen adsorbed on the surface and from surface zirconium. Also, oxygen

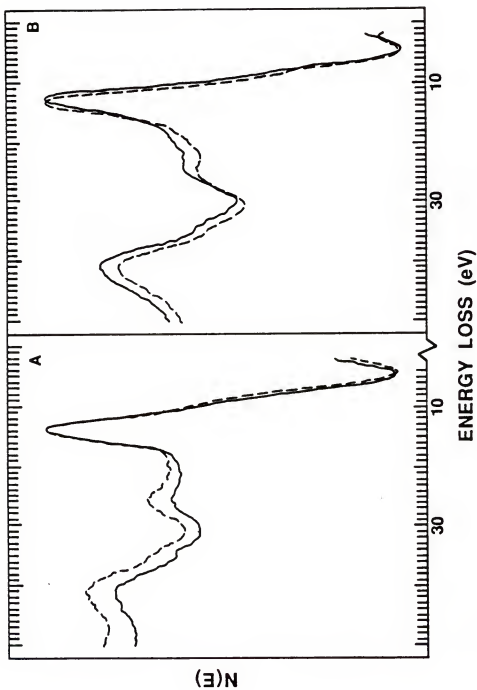


Figure 3-3. ELS spectra obtained using primary beam energies of (A) 200 eV and (B) 600 eV. The dashed-line ELS spectra were taken from a 40 L oxygen-exposed surface, and the solid-line ELS spectra were taken from a 2000 L hydrogen pre-exposed, 40 L oxygen-exposed surface.

desorbs as both O^+ and OH^+ species. From these results it was postulated that a surface oxide, a surface hydride and a surface hydroxide are present. Furthermore, the relative concentrations of the surface species vary with sample history.

In agreement with the ESD results, evidence of species other than an oxide can be found in the ELS spectra from the hydrogen pre-exposed surface. In figure 3-3A the intensity of the 14.0 eV feature is increased relative to the intensity of high energy loss features in the hydrogen-dosed/oxygen-dosed spectrum. Since the major loss feature from both a hydrogen-exposed surface and an oxygen-exposed surface is a peak at 14.0 eV, the increase in this feature for a hydrogen-dosed/oxygen-dosed surface compared to an oxygen-dosed surface suggests the possibility of the coexistence of a hydride and an oxide. Further evidence for the presence of a hydride may be found from the reduction in intensity of the 25 eV loss feature relative to the shoulder between 18 and 22 eV loss energy in figure 3-3A and 3-3B. The 25 eV loss feature is tentatively identified as a plasmon loss feature in the oxide (65). It is present in oxide loss spectra but not hydride or clean metal spectra. In the hydride spectra a shoulder between 18 and 25 eV loss energy is clearly present. Thus, the addition of a hydride loss spectrum to an oxide loss spectrum would tend to cause a reduction in the relative intensity of the 25 eV loss feature associated with the oxide compared to the intensity between 18 and 22 eV loss energy. However, the presence of a hydroxide species may alter this interpretation. Thus, the suggestion that a hydride and an oxide coexist in the surface region

can only be made tentatively. However, it is clear from figure 3-3 that there are differences between the hydrogen-exposed/oxygen-exposed spectra and the oxide spectra.

Additionally, the presence of a hydride prior to oxygen dosing seems to result in a decrease in the uptake of oxygen or lessen the interaction between the oxygen and zirconium. This can be seen in figure 3-4 which depicts the low loss energy region of the ELS spectra from oxygen-dosed (3-4A) and hydrogen-dosed/oxygen-dosed (3-4B) surfaces. A detailed interpretation of the loss spectra between 1 and 4 eV loss energy for partially oxidized zirconium has been given previously (65). Two loss features at about 1.5 eV loss energy and between 2 and 4 eV loss energy combine to give the observed line shapes. The disappearance of the 1.5 eV loss feature resulting in the "peak-like" line shape is evidence of an increase in the oxidation state of the zirconium. Thus, as the spectra vary from a straight line to the "peak-like" line shape, the oxidation state increases. By comparing figures 3-4A and 3-4B, it is apparent that the oxidation state of the oxygen-exposed surface region is continually increasing with depth whereas the oxidation state of the hydrogen-exposed/oxygen-exposed surface region reaches a maximum near the depth probed by the 400 eV primary beam. This means that either less oxygen adsorbs at the hydrogen-predosed surface or that the oxygen present is interacting with the hydrogen thereby lessening the interaction with the Zr.

Further evidence of the reduced uptake of oxygen or the reduced O/Zr interaction on the hydrogen-predosed surface is gained by

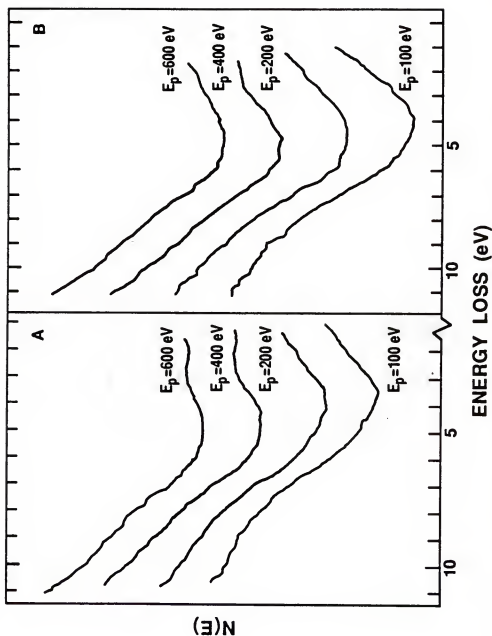


Figure 3-4. Enlargement of the low-energy-loss region of ELS spectra obtained from (A) the 40 L oxygen-exposed and (B) the 2000 L hydrogen-pre-exposed, 40 L oxygen-exposed surfaces. The spectra were obtained using primary beam energies of 100, 200, 400 and 600 eV. The spectra from the 40 L oxygen-exposed surface are reproduced from reference 65.

considering shifts in the band gap with varying probed depth. The band gap can be estimated by extending the low loss energy side of the 9 eV shoulder to the baseline. Also, the band gap can be considered to be a crude measure of the oxidation state of the zirconium surface region (12). As the band gap varies from 0 to 7 eV the oxidation state of the zirconium varies from 0 to +4. Thus, by comparing figures 3-4A and 3-4B it can be seen that the band gap of the oxygen-exposed surface continually increases with probed depth from 4.6 eV for $E_p = 100$ eV to 6.1 eV for $E_p = 600$ eV. Conversely, the band gap of the hydrogen-predosed surface reaches a maximum of 5.8 eV at the depth probed by the 400 eV primary beam (approximately 20 Å).

Conclusions

A detailed interpretation of the first electron energy loss data of hydrogen-exposed and hydrogen-exposed/oxygen-exposed polycrystalline zirconium has been presented. Hydrogen is readily detectable using ELS, and by varying the primary beam energy, the depth of the hydrided layer formed can be estimated. Following a 2000 L dose of hydrogen at 770 K, the depth of the hydrided layer is estimated to be between 30 and 40 Å. Differences in the ELS spectra taken from an oxygen-dosed zirconium surface and an oxygen- and hydrogen-dosed zirconium surface suggest that less oxygen adsorbs on a hydrogen predosed surface and/or the adsorbed oxygen interacts less with the zirconium due to an interaction with hydrogen.

CHAPTER IV
OXYGEN UPTAKE AND CO ADSORPTION ON
POLYCRYSTALLINE ZIRCONIUM

Introduction

This study is part of a continuing effort to understand the interaction of simple gases including H_2 , D_2 , O_2 , N_2 , CO and N_2O with polycrystalline zirconium (1,3,4,17,59,65,72). These species readily dissociate on zirconium at room temperature and then migrate into the bulk at varying rates depending upon the temperature (8). Hydrogen and deuterium are the only species which desorb thermally (59,17,8). Using electron stimulated desorption (ESD), it has been shown that surface hydrogen is always present on polycrystalline zirconium in varying quantities depending upon sample pretreatment (1). Furthermore, this surface hydrogen chemically associates with adsorbed oxygen when it is present.

The fact that most adsorbed species migrate into the bulk zirconium suggests that it would be of interest to utilize techniques of varying surface sensitivities to characterize their distribution as a function of depth. Thus, ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (ELS) have been used in this study to examine the adsorption of O_2 and CO on polycrystalline zirconium. ISS is the most surface sensitive of these techniques probing only the outermost one or possibly two atomic layers. Generally, AES and XPS are less surface sensitive, but this varies

depending upon the spectral features being examined, the type of material being studied and the experimental geometry used. The surface sensitivity of ELS depends upon the primary electron beam energy and the experimental geometry. ELS varies from being highly surface sensitive to essentially being bulk sensitive (34,65,72). The purpose of this study is to investigate the room-temperature adsorption of oxygen as a function of exposure using techniques of varying surface sensitivities and to describe the manner in which CO bonds to the surface after adsorption at room temperature.

Experimental Procedure

A polycrystalline zirconium foil of approximate dimensions 15 x 10 x 0.12 mm and 99.99% purity was used in this study. The sample was etched in a hydrofluoric acid solution in order to remove most of the accumulated oxide layer. Then it was solvent cleaned in ethanol and spot welded onto two 0.020 in. tungsten support wires. A tungsten filament placed behind the sample was used to heat the sample radiantly or by electron bombardment. Sample temperatures were measured using an optical pyrometer in order to avoid contamination by thermo-couple materials (4).

The experiments were carried out in an ultrahigh vacuum system which had a base pressure of 2×10^{-10} Torr in this study. AES, XPS, ELS and ISS were performed using a double-pass cylindrical mirror analyzer (CMA) (PHI Model 15-255 GAR) which contained an internal electron gun and a movable angularly resolving aperture. The sample was tilted at an angle of 45° with respect to the axis of the

analyzer. AES was performed in the nonretarding mode with a primary beam energy of 3 keV and an oscillation voltage of 0.5 V_{pp}. ELS was done in the retarding mode using pulse counting at a total energy resolution of about 0.8 eV. The primary beam energy was varied from 100 to 600 eV. XPS was performed using a PHI X-ray source with a Mg anode and a total resolution of about 1.0 eV. A PHI sputter gun was used both for inert-gas ion bombardment and for ISS. ISS was performed in the nonretarding mode using 1 keV He⁺ ions and a scattering angle of 100°. Since AES, ELS and ISS all cause beam damage at the surface, efforts were made to minimize the total dose but still obtain reasonable signal-to-noise ratios.

Results and Discussion

Oxygen Uptake Experiments

After cleaning the sample oxygen adsorption experiments were performed as a function of exposure. The exposures were carried out at room temperature, and the sample was cleaned by sputtering and annealing between each exposure. The oxygen uptake results as determined by ISS, AES and XPS are shown in figure 4-1 (a), (b) and (c) respectively. The ordinate scale is indicated for each curve, but the curves are arbitrarily scaled with respect to each other. The ISS O/Zr peak-height ratio is plotted in (a), the AES O (515 eV)/Zr (92 eV) peak-height ratio is plotted in (b) and the XPS O 1s/Zr 3d peak-area ratio is plotted in (c). The ISS results indicate a rapid uptake between 0 and 0.75 L, a plateau region between 0.75 and 2 L and a slower uptake between 2 and 6 L. Saturation coverage

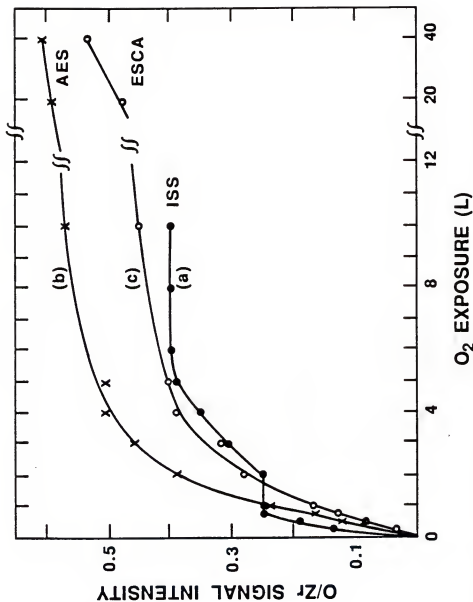


Figure 4-1. Oxygen uptake as a function of room-temperature oxygen exposure as determined by (a) ISS, (b) AES and (c) XPS. The O/Zr peak-height ratio is plotted in (a), the O (515 eV)/Zr (92 eV) peak-height ratio is plotted in (b) and the O 1s/Zr 3d peak-area ratio is plotted in (c). The ordinate scale is indicated for the ISS results. The XPS and AES scales are 2 and 4 times these values respectively, but the scaling of the curves with respect to each other is arbitrary.

is attained at 6 L according to ISS. The uptake according to AES is more gradual over a broader range of exposure. It appears that a change in slope occurs at 0.75 L and that saturation is not reached at 40 L. These results seem to be consistent with those of Sanz et al. (10). In their study a large number of data points were taken, and a mechanistic analysis of the data is presented. The XPS results shown in (c) are quite similar to the AES results except that no discontinuity in slope is observed in the low exposure region and the rate of adsorption is greater in the 20 to 40L exposure range.

It is difficult to make a quantitative comparison of the three curves presented in figure 4-1 because both depth sensitivity and oxygen concentration are difficult to quantify for all three techniques. However, a qualitative comparison based on the facts that ISS is much more surface sensitive than either AES or XPS and that, in these experiments, AES is somewhat more surface sensitive than XPS yields insight into the low-pressure room-temperature interaction between oxygen and polycrystalline zirconium. The rapid initial uptake observed using ISS suggests that oxygen readily adsorbs on a clean zirconium surface and populates the outermost layer. The plateau region in the ISS adsorption curve is not understood, but a speculative interpretation can be given. It is possible that the plateau region can be associated with disruption of the lattice or the formation of an oxide lattice comprising the first atomic layer of the zirconium. This lattice may allow more freely the transport of oxygen to beneath the surface. This increase in oxygen transport to the subsurface can be seen as an increase in the slope of the AES

adsorption curve where the ISS plateau region lies in figure 4-1. The further uptake observed using ISS following the plateau region may be due to the subsurface region near the surface beginning to saturate with oxygen. This saturation may cause a decrease in the rate of oxygen transport to the subsurface and allow more surface sites to fill. It is clear that the surface sites fill much more slowly after the plateau region than before it. These results also imply that after the new lattice has formed oxygen would rather lie beneath the surface. An alternative interpretation of the plateau region in terms of binding sites where one binding site fills initially and another fills after the plateau does not seem plausible. This is because the increase in oxygen uptake at the exposure where the plateau occurs has been seen on a sputtered polycrystalline zirconium surface using AES by Sanz et al. (10) and on a Zr(0001) surface using XPS by Tapping (7). In this study a well annealed polycrystalline surface was studied. The binding site argument is not plausible since similar binding sites would unlikely be active on the three different zirconium surfaces studied.

Using both AES and XPS it is clear that adsorption continues over the 20 to 40 L range. However, the rate of adsorption in this exposure region as determined with XPS is greater than that for AES. This indicates that the region probed using AES is becoming saturated, but the deeper region probed by XPS continues to become populated. These techniques provide evidence that the oxidation of polycrystalline zirconium proceeds in stages and that oxygen penetrates beneath the surface layer of atoms forming a multilayer oxide film at room temperature.

CO Adsorption

An Auger spectrum obtained after exposing the clean zirconium surface to 2500 L of CO at room temperature is shown in figure 4-2. Large carbon and oxygen peaks are present. In contrast, using ISS only peaks associated with oxygen and zirconium are observed as is shown in figure 4-3. This implies that the carbon penetrated beneath the outermost layer leaving an oxide layer at the surface. Further support for this interpretation has been obtained using ELS. In figure 4-4 four ELS spectra are presented with varying primary beam energies from 100 to 600 eV which were obtained following an exposure of 4000 L of CO. In the most surface sensitive of these spectra, where the primary beam energy is 100 eV, the loss features are essentially identical with those obtained following oxygen exposure (65). However, by increasing the primary beam energy and thus the probed depth, loss features near 20 eV which can be associated with the excitation of the C 2s level increase in intensity. These results suggest that carbon lies beneath an oxide-rich surface layer.

The AES carbon peak shape in figure 4-2 is indicative of molecularly bound CO (73). However, the XPS C 1s peak lies at 282.2 eV which is indicative of a carbidic species and clearly not CO. Heating the sample to a few hundred degrees Centigrade rapidly converts the AES carbon peak shape to that of a carbide (73) and reduces the size of the AES oxygen peak through segregation of oxygen into the bulk. The XPS O 1s peak lies at 530.5 eV before heating which is indicative of an oxide species and not that of oxygen bonded to carbon.

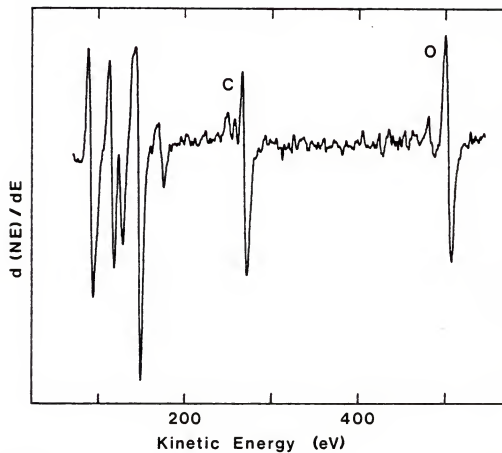


Figure 4-2. AES spectrum taken after exposing the clean zirconium surface to 2500 L of CO at room temperature.

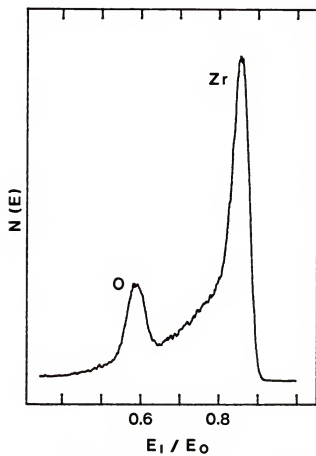


Figure 4-3. ISS spectrum corresponding to the AES spectrum shown in figure 4-2.

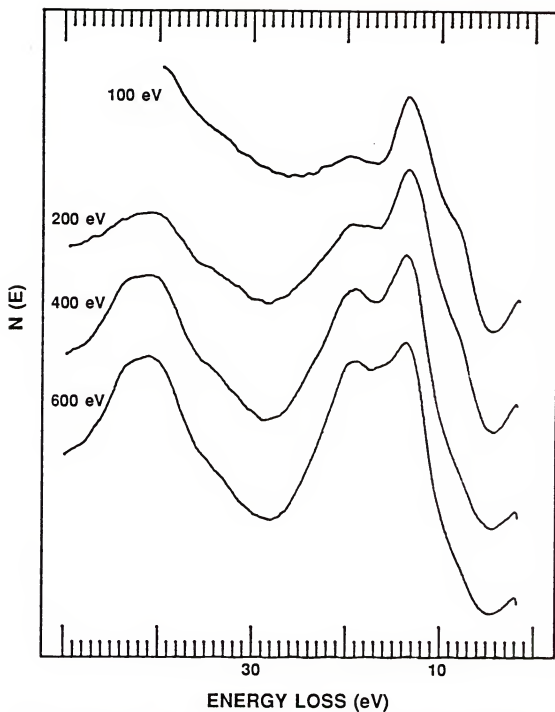


Figure 4-4. ELS spectra obtained from polycrystalline zirconium following a 4000 L exposure of CO. The primary beam energies used are 100, 200, 400 and 600 eV.

These data suggest that CO adsorbs on zirconium dissociatively at room temperature forming an oxide-rich surface layer with the carbon penetrating beneath the surface. The carbon is probably bonded interstitially in the zirconium lattice but forms a carbide when heated. This suggests that an activation barrier must be crossed in going from interstitially bonded carbon to a zirconium carbide.

Conclusions

ISS, AES and XPS have been used to examine the chemisorption of oxygen as a function of exposure at room temperature. ISS shows that oxygen rapidly adsorbs at the outermost atomic layer. AES and XPS data combined with the ISS results show that oxygen also penetrates beneath the surface forming a multilayer oxide film. ISS shows that the outermost surface layer becomes saturated at an exposure of 6 L while AES and XPS show that the near-surface region is not saturated even at an exposure of 40 L.

AES shows that a room-temperature, 2500 L exposure to CO results in significant adsorption of CO. The adsorption is dissociative as demonstrated by XPS. The outermost layer consists of an oxidic layer, and the carbon lies beneath the surface. This carbon is probably in an interstitial or chemisorbed form but converts to a carbide upon heating to a few hundred degrees Centigrade.

CHAPTER V
AN ELECTRON ENERGY LOSS STUDY OF
CLEAN AND OXYGEN-EXPOSED POLYCRYSTALLINE TIN

Introduction

It is important to understand the surface oxidation behavior of tin because of the many uses of tin ranging from its use in semiconductor devices (74,75) to bimetallic catalysts (76-79). Hence, the oxidation of tin has been studied by a number of authors (34,80-95). These studies have led to controversy as to the oxidation state of tin in the surface region following oxygen exposures because of the difficulty in distinguishing between the two common oxidation states of tin, SnO and SnO_2 . Using XPS, it is possible to distinguish between metal and oxide; the tin metal $3d_{5/2}$ feature is at 484.65 eV binding energy and the oxide $3d_{5/2}$ feature is at 486.4 eV binding energy, but no binding energy difference is observed between the two oxidation states (80-82). Using valence-band XPS or UPS it is possible to distinguish between the oxidation states of tin (80,86,87,34). However, it is difficult to apply these techniques in an effort to obtain chemical state depth profiles due to the long mean free paths of the collected electrons (71) and the inability to vary these mean free paths over a wide range.

AES has also been used to study the tin-oxygen interaction (81,87,90,92,94). However, as with XPS, identical Auger chemical shifts for SnO and SnO_2 have been observed, although the amount of the shift for the $M_4N_{4,5}N_{4,5}$ and the $M_5N_{4,5}N_{4,5}$ Auger transitions has

varied with different studies. Asbury and Hoflund (94) and Lin et al. (81) observed a shift of 5 eV from metal to oxide, whereas Powell (87) observed a shift of 5.5 eV and Wagner and Biloen (92) measured 3.9 eV. Contrary to these studies Sen et al. (90) observed a shift of 3 eV for SnO and a shift of 7 eV for SnO₂. Also, based on N(E) AES results, Asbury and Hoflund (94) suggest that tin may exist in a well defined oxidation state less than +2 following low pressure exposures.

It is evident from the variations in spectra from different laboratories and the difficulty in distinguishing between the common oxidation states of tin that XPS and AES are not the best choices for primary techniques for studying tin oxidation. The technique that seems to offer promise for studying the oxidation of tin is ELS. ELS is sensitive to both the occupied and unoccupied density of states near the Fermi level and thus offers the ability to distinguish between the oxidation states of tin. Also, by using reflection ELS and varying the primary beam energy and/or the experimental geometry, depth-sensitive chemical-state information can be obtained. ELS has been used by Woods and Hopkins (93), Bevelo et al. (85), Stander (91) and Powell (87) to study the oxidation of tin. However, the interpretations of the results are quite varied. Woods and Hopkins (93) used ELS with a single primary beam energy of 70 eV combined with AES and LEED. They suggest that following a low-pressure, room-temperature, saturation dose of oxygen (approximately 2500 L), a single monolayer of SnO is formed on the surface. Bevelo et al. (85) present limited depth-sensitive ELS data taken using two primary beam

energies, 75 eV and 400 eV, and varying the incident angle. They suggest that continuous oxide films free of metallic tin are grown following oxygen exposures of $100 - 10^7$ L. They also propose that SnO_2 and SnO are present in any oxide layer grown and that the surface is SnO_2 rich. Furthermore, the authors observe the simultaneous presence of a surface plasmon for both the metal and the oxide based on which they propose that following exposures of less than 100 L island growth of the oxide occurs. Powell (87) combined UPS, XPS, AES and work function measurements with ELS using a single primary beam energy of 400 eV. Based on results using these spectroscopies Powell proposed that a metallic surface may be present following low-pressure exposures below which lies primarily SnO with some SnO_2 . Based on ELS results using a single primary beam energy of 435 eV, Stander (91) proposed that a highly non-stoichiometric SnO_2 oxide layer is formed during the initial stages of oxidation. Stander also supports Powell by proposing that a metal-rich surface layer is formed and further postulates that this layer is composed of a high concentration of tin interstitials.

Although the above authors differ greatly in their description of the nature of the tin-oxygen interaction, they do demonstrate that ELS is a powerful technique for studying tin oxidation because the common oxidation states can be distinguished and depth-sensitive information is easily obtainable. It is clear, however, that a more detailed ELS study is needed in which the primary beam energy, experimental geometry and oxygen exposures are varied over a wide range. The work presented below is such a study, and a more through

understanding of the oxidation of tin as a function of exposure and depth is presented.

Experimental Procedure

A polycrystalline tin foil (7 x 10 x 0.25 mm) of 99.9995% purity was used in this study. The sample was solvent cleaned in toluene, trichloroethylene, acetone and ethanol prior to insertion into an ultrahigh vacuum chamber.

This study was performed in two separate ultrahigh vacuum (UHV) systems (base pressures of 2×10^{-10} Torr). These systems have been described elsewhere (45,96). ELS, AES and ISS spectra were collected using PHI double-pass cylindrical mirror analyzers (PHI model 15-255GAR and PHI model 25-270AR). ELS was performed in the retarding mode using pulse counting (46) and a pass energy of 25 eV ($\Delta E/E_{\text{pass}} = 0.016$). Ten 2000 channel spectra over a 50 V range were taken with a maximum count rate of 8,000 counts/channel each. The summation of these spectra was then averaged with a spline quadratic fit to obtain the presented ELS spectra. A primary beam current of 100 nA over a spot size of approximately 0.1 mm was used. The full width at half maximum (FWHM) of the elastic peak decreased from 0.82 eV at $E_p = 600$ eV to 0.52 eV at $E_p = 100$ eV. Angle-resolved ELS spectra were obtained using both the CMA electron gun and an auxiliary electron gun combined with the angle-resolving movable aperture in the CMA. In the angle-integrated or all angles collection mode, electrons were collected in a 360° cone which, with its point on the sample, makes an angle of approximately 42.3° with respect to the CMA electron

gun. Many of the ELS experiments were performed in both vacuum systems and the ELS spectra were found to be very reproducible.

AES and ISS spectra were obtained by operating the CMA in the nonretarding mode. AES was performed using a 3 KeV primary beam energy. Lock-in detection was used with a 0.5 V_{pp} sine wave of 10 kHz applied to the outer cylinder of the CMA. ISS was performed using 1 keV He⁺ ions and pulse counting. The movable aperture and the sample position were adjusted so that the scattering angle was approximately 100°. Data collection time and emission were minimized to reduce sputtering effects. These effects were found to be negligible by AES which was taken before and after ISS spectra were obtained.

Results and Discussion

ELS Depth Sensitivity

To determine the depth sensitivity of each ELS experiment the first order term in the poisson distribution must be used:

$$P(1) = (d/\lambda)e^{-(d/\lambda)} . \quad (5-1)$$

This term can be related to the probability that one inelastic collision will occur in depth d where λ is the inelastic mean free path. In addition to mean free path considerations, the intensity of spectral features in energy loss spectra are a strong function of electronic or chemical state variations in the surface region and can be a strong function of the primary beam energy due to cross-section

variations. Thus, it is difficult to determine if, for example, a reduction in a metal feature upon oxygen exposure is due to the formation of an oxide overlayer or to these other effects. Therefore, a quantitative depth profile determined by deconvolution is difficult using ELS data; however, it is possible to obtain a semiquantitative depth profile. Such a depth profile is given below for the oxidation of tin. To determine this depth profile the sampling depth of each primary beam energy is determined. This depth is defined here as the depth from which 95% of the inelastically scattered electrons are collected. Taking into account the experimental geometry used here and equation (5-1), the sampling depth is given by

$$d = \frac{(4.5) \lambda \cos(X) \cos(Y)}{\cos(X) + \cos(Y)} \quad (5-2)$$

where X is the incident angle and Y is the collected angle with respect to the sample normal.

Clean Polycrystalline Tin

In order to obtain a clean surface the sample was argon-ion sputtered for four hours. A 2 keV beam energy was used with an approximate beam current at the sample of 1 uA over an area of about 2 mm. An AES spectrum of the resulting surface is shown in figure 5-1. The only features detected are those of tin. Electron energy loss spectra taken from the cleaned polycrystalline tin surface are shown in figure 5-2. Four spectra are presented which were obtained with primary beam energies of 200, 400 and 600 eV. The bottom two

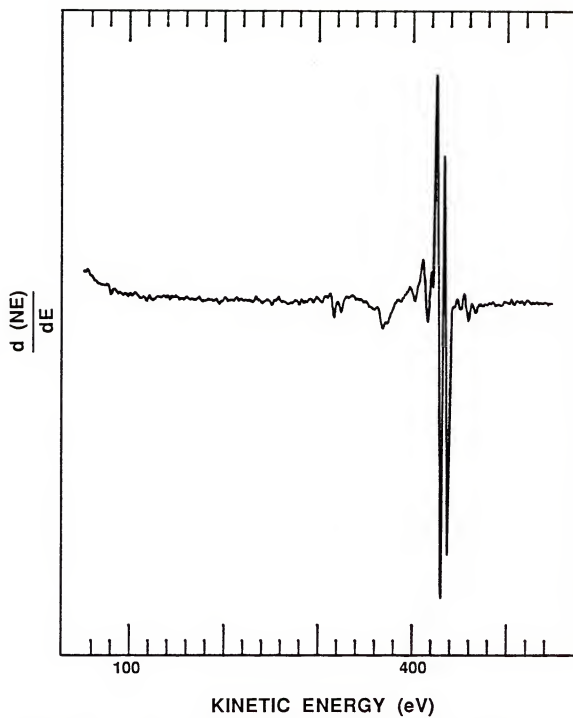


Figure 5-1. An AES spectrum of sputter cleaned polycrystalline tin.

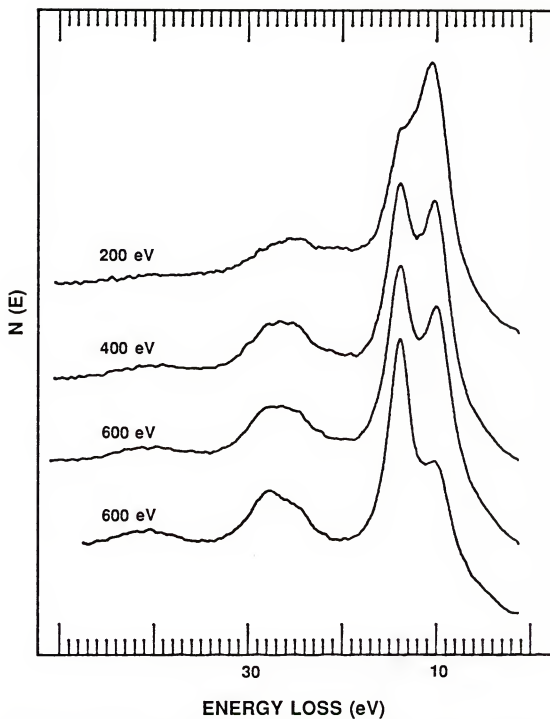


Figure 5-2. ELS spectra taken from sputter cleaned polycrystalline tin using primary beam energies of 200, 400 and 600 eV.

spectra were each obtained with $E_p = 600$ eV but different experimental geometries were used. In the upper $E_p = 600$ eV spectrum, as for the 200 and 400 eV spectra, the sample was tilted 45° with respect to the CMA electron gun and all angles were collected. The lower 600 eV spectrum was obtained with the sample normal parallel to the CMA electron gun and all angles were collected. These spectra agree well with those presented by Bayat-Mokhtari et al. (95). Angle-resolved electron energy loss spectra have also been obtained from the cleaned surface and are depicted in figure 5-3. Spectra 5-3(a) and (c) were obtained with an 80° incident angle and an 80° collection angle (all angles are specified with respect to the sample normal unless otherwise stated), and spectra 5-3(b) and (d) were acquired with an 80° incident angle and a 0° collection angle. Further, spectra 5-3(a) and (b) were obtained using a 200 eV primary beam energy, and spectra 5-3(c) and (d) were obtained with $E_p = 600$ eV. Using expression (5-2) and the mean free path data compiled by Seah and Dench (71), the sampling depths for the various primary beam energies and experimental geometries for the cleaned surface have been determined and are given in Table 5-1.

The interpretation of the energy loss data acquired from the cleaned surface shown in figures 5-2 and 5-3 is as follows. The weak shoulder near 5 eV loss energy is due to an interband transition (95) and is probably associated with a transition between the Sn 5s level and the unoccupied Sn 5p level. The two main loss peaks, one at approximately 10.5 eV and the other at 14.0 eV loss energy, are associated with a surface and bulk plasmon excitation respectively

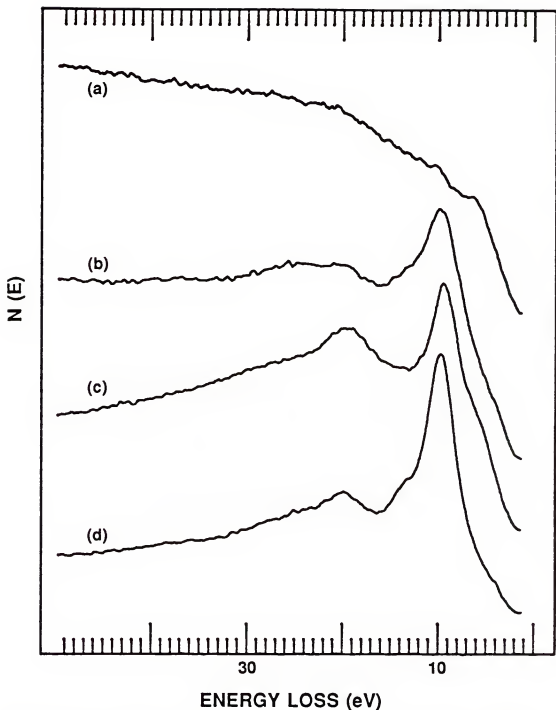


Figure 5-3. Angle-resolved ELS spectra taken from sputter cleaned polycrystalline tin. Spectra (a) and (b) were obtained with $E_p = 200$ eV, and spectra (c) and (d) were obtained with $E_p = 600$ eV. Spectra (a) and (c) were obtained with $X = 80^\circ$ degrees and $Y = 80$ degrees, and spectra (b) and (d) were obtained with $X = 80$ degrees and $Y = 0$ degrees.

Table 5-1. ELS Sampling Depths for Clean Tin

<u>E_p(eV)</u>	<u>λ(nm)</u>	<u>Sampling Depth; 45° incident Angle-integrated collected (nm)</u>
100	0.7	1.0
200	1.0	1.3
400	1.4	1.9
600	1.6	2.3
Sampling Depth; 0° incident <u>Angle-integrated collected (nm)</u>		
600	1.6	3.2

Angle-resolved ELS
Sampling Depths for Sn (nm)

<u>E_p(eV)</u>	<u>X = 80° Y = 80°</u>	<u>X = 80° Y = 0°</u>
200	0.4	0.6
600	0.6	1.1

(95,97,98). These peaks follow the classical behavior of plasmon excitations with varying primary beam energy and experimental geometry. In figure 5-2 the peak at 10.5 eV is seen to markedly decrease with increasing probed depth. In contrast, the 14.0 eV peak in figure 5-2 increases relative to the 10.5 eV peak with decreasing surface sensitivity. The surface plasmon peak is also observed to shift from 10.7 to 10.1 eV by varying the primary beam energy from $E_p = 200$ to 600 eV. The bulk plasmon peak does not seem to vary with varying primary beam energy. Bayat-Mokhtari et al. (95), however, observe the bulk plasmon peak to increase from 13.7 to 14.1 eV upon increasing the primary beam energy from 100 to 1000 eV. Also, although they do not state it, it is clear from their data that the surface plasmon peak is also shifting in a similar fashion as that seen here. It is proposed by Bayat-Mokhtari et al. (95) that the shift in the bulk plasmon peak can at least in part be attributed to plasmon dispersion. Similarly, the shift in the surface plasmon may be attributed to dispersion (39). By varying the primary beam energy the momentum transfer to the scattering electron varies (65) which should result in a similar dispersion as that observed in transmission ELS by varying the collection angle.

The large, broad loss feature between 23 and 32 eV loss energy can be chiefly attributed to multiple plasmon excitations which are surface-bulk and bulk-bulk plasmon combinations. This interpretation is based on the line shape variation of this loss feature with varying probed depth and can be best seen in figure 5-2. The line shape closely follows the variation in the intensity of the plasmon

excitations as a function of sampling depth. The intensity at 24 eV loss energy decreases relative to the intensity at 28 eV with increasing probed depth. In addition, in the 600 eV angle-resolved spectra shown in figure 5-3(c) and (d) a broad peak centered near 20 eV is visible. This feature can be attributed to a double-surface plasmon excitation since the intensity of this feature seems to be a function of probed depth and experimental geometry only. The inability to resolve this peak in the 200 eV spectra of figure 5-3 is probably due to the large background. In figure 5-2 the intensity at 20 eV relative to the background continually increases with decreasing probed depth. Further, from figure 5-3 the intensity of the 20 eV peak increases relative to the 10 eV peak when both the incident and the collected beams are near grazing the surface.

Note also from figure 5-3 the long shoulder on the high energy side of the 20 eV peak. The major contributor to the broad 28 eV loss peak in the non-angle-resolved spectra is a double bulk-plasmon excitation and in the angle-resolved spectra the bulk-plasmon loss feature is nearly absent. This shoulder in the angle-resolved spectra may be the result of an interband transition from the Sn 4d level to the unoccupied portion of the Sn 5p level. This single particle excitation seems to have a small cross section for the cleaned surface, but it is clearly visible in the ELS spectra obtained from the oxygen-exposed surface (shown below).

In addition, very low energy ELS (<150 eV) appears to be sensitive to surface roughness. In this study the cleaned surface was obtained by sputtering, and a 100 eV energy loss spectrum of this

surface is shown in figure 5-4. It is clear that this spectrum is not consistent with those spectra in figures 5-2 and 5-3, although this 100 eV spectrum is very reproducible. Since the sampling depth is only 1 nm, the lack of a distinct surface plasmon feature near 10 eV, although a weak shoulder is present, suggests that the surface atoms are so disrupted that the valence bands are not formed in a well-defined manner. In contrast, Bayat-Mokhtari et al. (95) obtained their clean surface by evaporating tin in vacuum onto a copper substrate. They show the surface plasmon excitation at 10 eV dominating their $E_p = 100$ eV spectrum. Evidently, evaporating tin in vacuum results in a less-disrupted surface layer. The presence of the surface plasmon loss in the $E_p = 100$ eV spectrum of Bayat-Mokhtari et al. (95) also demonstrates that the disappearance of this loss feature in the spectrum presented here cannot be explained in terms of a critical momentum transfer (39,65).

The spectrum in figure 5-4 is made up of a weak shoulder near 10 eV, a prominent peak at 14.5 eV and a broad peak from 25 to 32 eV. A possible interpretation of these features is that the 14.5 eV peak is due to an interband transition from the Sn 5p level to the Sn 6s unoccupied level. The excitation of the Sn 4d level may be associated with the broad 29 eV peak, and the 10 eV shoulder may be due to the surface plasmon excitation. This suggests that the valence bands which give rise to the surface plasmon excitation lie approximately 1 nm beneath the outermost surface atoms on this sputtered surface. Another view of this is that the sputter damage is approximately 1 nm thick. It is not clear why in the angle-

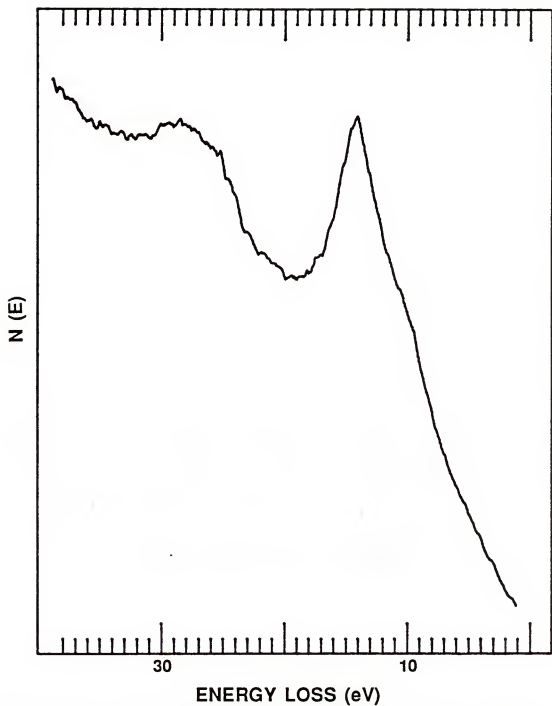


Figure 5-4. $A E_p = 100$ eV ELS spectrum taken from sputter cleaned polycrystalline tin.

resolved spectra the surface roughness was not detected to the same extent as in the $E_p = 100$ eV spectrum.

Oxygen-exposed Polycrystalline Tin

In interpreting ELS spectra an understanding of the joint density of states (JDOS) near the Fermi level is useful. However, in general, during the initial stages of oxidation a mixture of oxidation states are present. Because of this mixture of oxidation states the JDOS in the surface region are complex, and thus the electronic nature of the surface region during the initial oxidation is difficult to determine from ELS spectra. Although in the case of tin during the initial oxidation a mixture of oxides are present, standard ELS spectra are available for the common oxidation states of tin (85,87). These standard spectra do not help in an electronic characterization of the surface region but do aid greatly in a chemical state determination of the surface region. The two sets of standard ELS spectra agree well with one another except that the SnO data given by Bevolo et al. (85) has a small SnO₂ contribution. The standard SnO and SnO₂ ELS spectra presented by Powell (87) which were obtained using a primary beam energy of 400 eV are reproduced in figure 5-5. The characteristic loss features of SnO are a peak near 9 eV, a broad peak near 14 eV and a small sharp peak near 27 eV loss energy. The loss features of SnO₂ are dominated by two peaks, one near 20 eV and a second near 13 eV loss energy. The loss feature near 27 eV loss energy seems to have less relative intensity in SnO₂ than in SnO. This decrease in intensity may be due to a change in

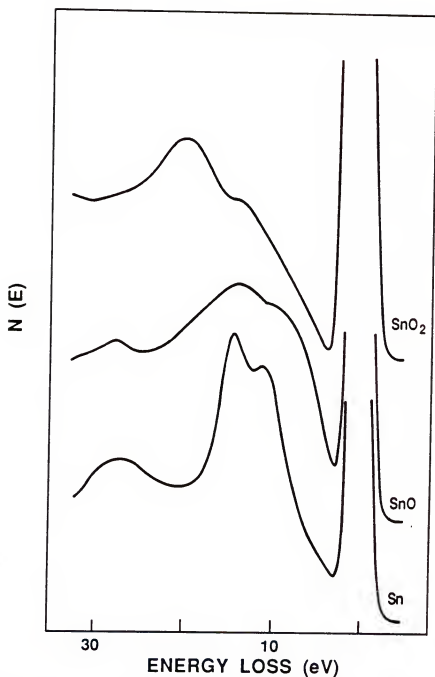


Figure 5-5. Standard ELS spectra for sputter cleaned polycrystalline tin, SnO and SnO_2 taken using a 400 eV primary beam. This spectra has been reproduced from Powell (87).

the conduction band minimum from Sn 5p to Sn 5s as the oxidation state varies from +2 to +4 (34).

Loss spectra interpretation

ELS spectra obtained from tin following low-pressure oxygen exposures of 100 L, 500 L, 1500 L and 3500 L are given in figures 5-6 through 5-9 respectively. The primary beam energy for each exposure is varied from 100 to 600 eV. Based on the mean free path data compiled by Seah and Dench (71), equation (5-2) and assuming an SnO surface region the depths probed using these primary beam energies have been determined and are presented in Table 5-2.

The spectral variations as a function of low pressure exposure can be more easily seen in figures 5-10 and 5-11. In figures 5-10 and 5-11 a portion of the tin energy loss spectra in figures 5-6 through 5-9 are presented as a function of oxygen exposure using primary beam energies of 200 and 600 eV respectively. Initially upon oxygen exposure, the peak at 10 eV is observed to quickly reduce relative to the 14 eV peak. This provides further evidence that the 10 eV peak of the clean metal results from a surface plasmon excitation since surface plasma oscillations vary rapidly due to adsorption because of dramatic changes in the surface valence-band electron density. With increasing low pressure exposures the 10 eV peak continues to decrease and a new feature at 9 eV loss energy appears. A steady shift in the 10 eV peak to 9 eV is not observed as is proposed by Stander (91). However, Stander used fewer exposures, and his data has much lower resolution than that presented here. A

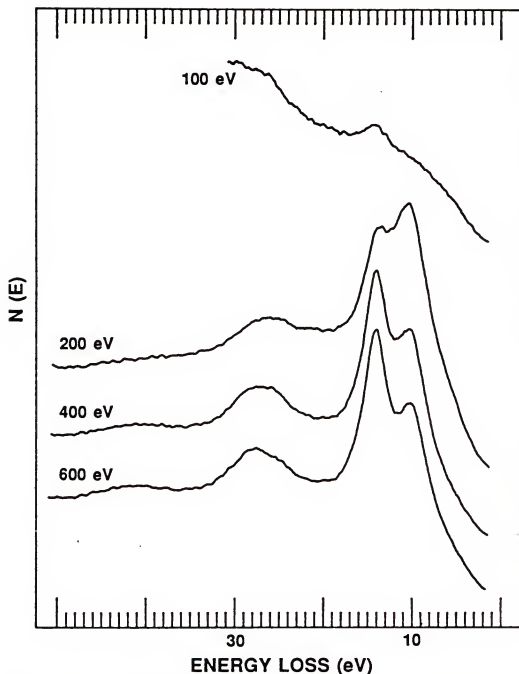


Figure 5-6. ELS spectra obtained from 100 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.

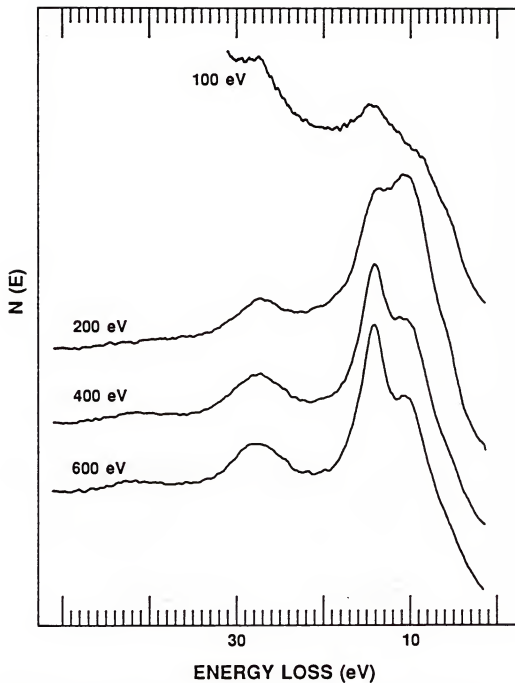


Figure 5-7. ELS spectra obtained from 500 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.

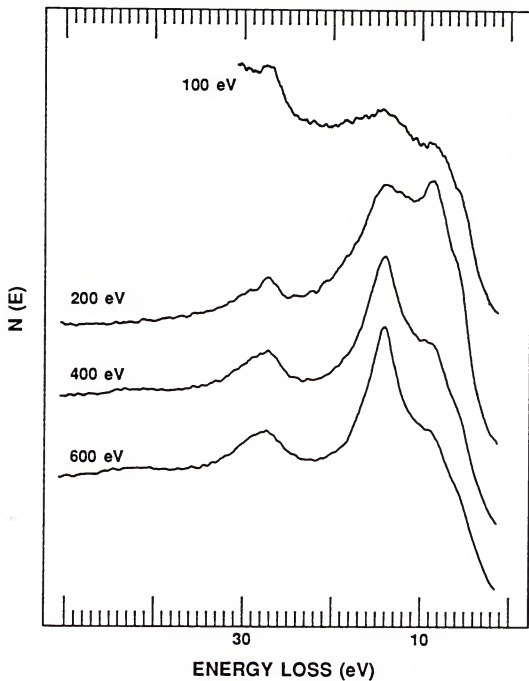


Figure 5-8. ELS spectra obtained from 1500 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.

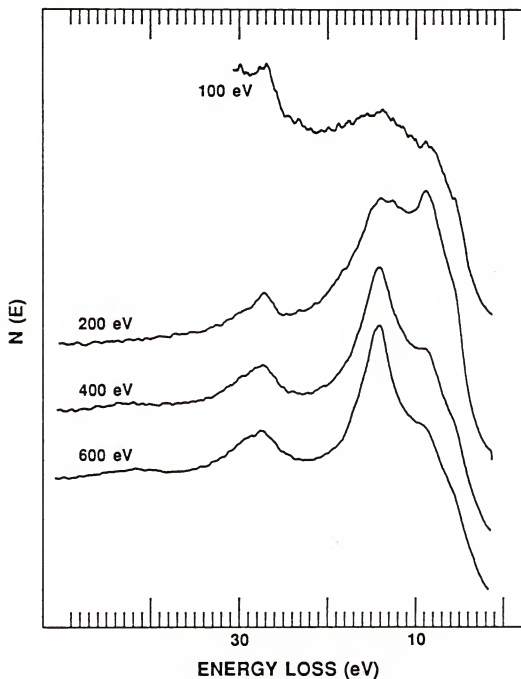


Figure 5-9. ELS spectra obtained from 3500 L oxygen-exposed polycrystalline tin using primary beam energies of 100, 200, 400 and 600 eV.

Table 5-2. ELS Sampling Depths for SnO

<u>E_p (eV)</u>	<u>λ (nm)</u>	<u>Sampling Depth</u> <u>Angle-integrated (nm)</u>
100	1.0	1.4
200	1.4	1.9
400	1.9	2.6
600	2.3	3.2

Angle-resolved ELS
Sampling Depths for SnO
 $E_p = 200$ eV

<u>Geometry</u>	<u>Sampling Depth (nm)</u>
X = 45° Y = 80°	0.8
X = 45° Y = 0°	2.5
X = 80° Y = 80°	0.5
X = 80° Y = 0°	0.9

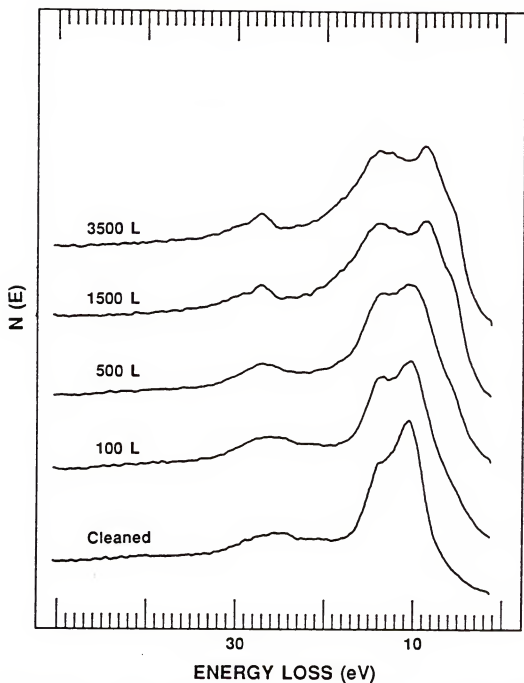


Figure 5-10. $E_p = 200$ eV ELS spectra obtained from the cleaned surface and from polycrystalline tin following oxygen exposures of 100, 500, 1500 and 3500 L.

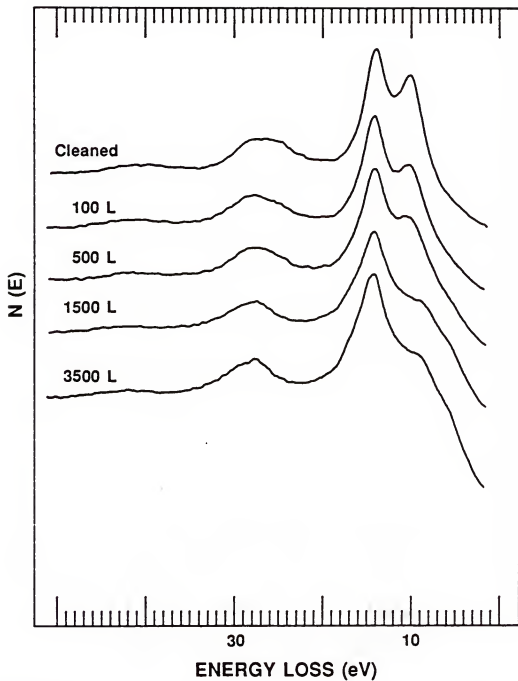


Figure 5-11. $E_p = 600$ eV ELS spectra obtained from the cleaned surface and from polycrystalline tin following oxygen exposures of 100, 500, 1500 and 3500 L.

shoulder at about 5.5 eV loss energy also appears following oxygen exposure and is observed to become more defined with increasing exposure. Also, the broad loss feature at 27.5 eV loss energy, which is associated with the excitation of multiple plasmons from the metal and an interband transition from the Sn 4d level, becomes more defined with increasing oxygen exposure. This increase in definition is probably due to an increase in the density of the final state for the Sn 4d interband transition combined with a decrease in the metal plasmon excitations. Based on a dipole-selection rule, the final state of the Sn 4d transition is likely to be the Sn 5p level (34). Furthermore, following oxygen exposures, small loss features between 10 and 14 eV loss energy appear and are probably due to excitations of the O 2p level. Again based on a dipole-selection rule, the final state for these excitations may possibly be associated with Sn 6s states.

An interpretation of the 5.5 eV shoulder appearing after low-pressure exposures has been proposed by Bevolo et al. (85). They suggest that this feature is associated with SnO_2 and is due to an excitation of the O 2p level. Based on dipole-allowed transitions the final state for this low energy transition from the O 2p level would be the Sn 5s level. However, as will be discussed further below, following low pressure exposures the tin in the surface region seems to be in approximately a +2 oxidation state in which the Sn 5s level is likely occupied (34). An alternative interpretation for this shoulder is that it can be attributed to a transition from the Sn 5s level to the unoccupied Sn 5p level. As stated above, this 5s

to 5p excitation is responsible for the low loss energy shoulder in the clean spectra, and it is probable that the resulting loss feature would become better defined as the 5p level becomes completely unoccupied as a result of oxidation.

There is some disagreement as to the nature of the excitation resulting in the main loss features of SnO and SnO₂. Powell (87) and Bevolo et al. (85) propose that these features are due to plasmon excitations, whereas, Cox and Hoflund (34) suggest that they can be attributed to single particle excitations. Based on the standard energy loss data of Powell (87) and Bevolo et al. (85), following low pressure exposures of greater than 1500 L, it is apparent that the tin is in approximately a +2 oxidation state within the depth probed using a 200 eV beam. To determine the nature of the excitations resulting in the main SnO loss features near 9 and 14 eV angle-resolved ELS using a 200 eV primary beam energy was performed. The incident angle used was 45° and the collection angles used were 80°, angle-integrated and 0°. The resulting spectra are shown in figure 5-12, and the sampling depths are given in Table 5-2. From figure 5-12 it is evident that as the surface sensitivity is increased the feature at 9 eV increases relative to the 14 eV loss feature. This provides evidence that the 9 and 14 eV loss features in SnO are indeed associated with a surface and a bulk plasmon excitation respectively since cross-section effects are removed by using a constant primary beam energy. Also from figure 5-12, the 9 eV feature (the surface plasmon excitation) is observed to shift between 8.5 and 9.0 eV which suggests that the oxidation state of the tin

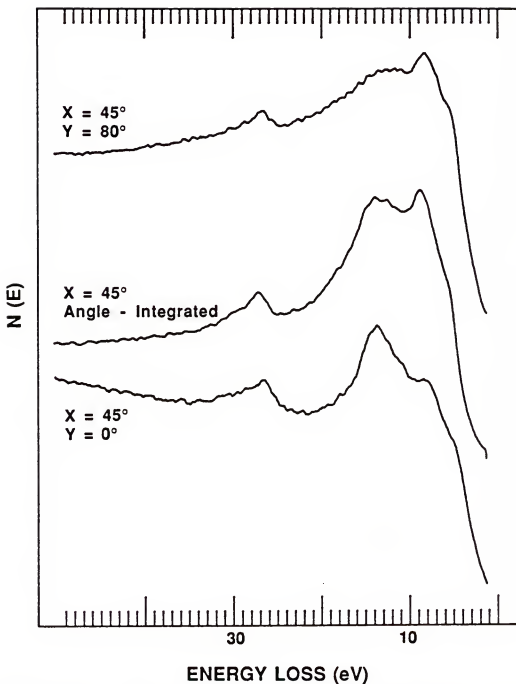


Figure 5-12. $E = 200$ eV angle-resolved ELS spectra obtained from polycrystalline tin following a 3500 L oxygen dose. The incident and collected beam angles are labelled.

varies and cannot be defined solely as +2. An explanation based on plasmon dispersion cannot be used in this case because the primary beam energy is constant.

To determine the nature of the excitations resulting in the 13 and 20 eV loss features of SnO_2 a distinct SnO_2 surface region is needed. However, no distinct loss feature at 20 eV, which is characteristic of SnO_2 , is observed following any of the low-pressure exposures. Furthermore, energy loss spectra obtained following high-pressure exposures reveal a mixture of oxidation states. A determination of the SnO_2 excitations from these spectra is complicated and cannot be unambiguously determined because of the presence of overlapping loss features from other oxidation states. The high-pressure exposed surface is discussed further below.

Using low energy ELS the change in the surface roughness can be followed as a function of oxygen exposure. In figure 5-13 four $E_p = 100$ eV loss spectra are presented which were obtained from a cleaned surface and a 50 L, 100 L and 500 L oxygen-exposed surface. Increasing exposure causes a reduction in the 14.5 eV peak and an increase in the 10 eV shoulder. It may be that the adsorption of oxygen "repairs" some of the damage caused by sputtering, probably by oxygen filling vacancies and/or by diffusion of tin to the oxygen-containing near-surface region. It is difficult to quantify this "repairing" process because, combined with this "restoration", the near-surface region is oxidizing. For example, although the surface plasmon at 10 eV increases following 50 and 100 L exposures, this excitation should decrease in intensity due to the adsorption of

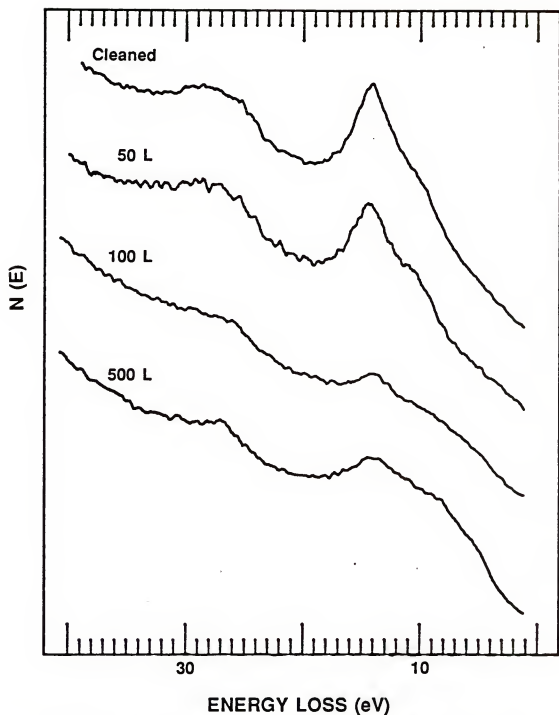


Figure 5-13. $E_p = 100$ eV ELS spectra obtained from the cleaned surface and polycrystalline tin following oxygen exposures of 50, 100 and 500 L.

oxygen. It is difficult to quantify the competition between oxygen adsorption causing the "restoration" of the surface, and thus increasing the metal surface plasmon intensity, and the adsorption of oxygen changing the valence band electron concentration, causing a reduction in the metal surface plasmon intensity. The oxidation of the near-surface region is easily seen in the 500 L spectrum which has features similar to SnO. Again, however, the surface plasmon loss feature for SnO at about 9 eV is reduced relative to the 14 eV bulk plasmon loss feature. This reduced SnO surface-plasmon loss feature is also seen following 1500 and 3500 L exposures for the $E_p = 100$ eV spectra (see figures 5-8 and 5-9). This implies that damage induced during sputtering is not completely "repaired" even following low-pressure saturation oxygen doses. Further evidence of this non-uniform surface layer is illustrated using ISS. Figure 5-14 has been reproduced from Asbury and Hoflund (94) and shows three ISS spectra obtained from sputter-cleaned tin, 3000 L oxygen-exposed tin and air-exposed tin. Using ISS, which is sensitive to essentially the outermost layer, only the presence of tin at $E/E_0 = 0.9$ is observed. Therefore, oxygen lies beneath the outermost tin atoms which results in a surface oxide different from that directly beneath it.

Oxidation state depth profile

The oxidation state of the tin as a function of oxygen exposure can be followed, and an ELS depth profile of the chemical state can be determined using the standard spectra of Powell (87) and Bevolo

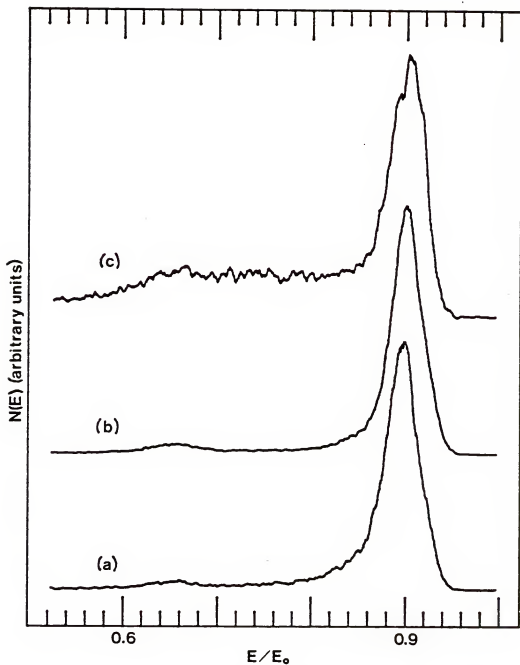


Figure 5-14. ISS spectra obtained from sputter cleaned polycrystalline tin, 3000 L oxygen-exposed tin and air-exposed tin. This data has been reproduced from Asbury and Hoflund (94).

et al. (85). Following exposures of 100 L or less, no distinct evidence of either SnO or SnO₂ is observed, yet a dramatic reduction in the surface plasmon excitation occurs. This reduction in the surface plasmon excitation suggests that the valence bands derived from the near surface tin atoms have been disrupted by the presence of oxygen. However, it appears that not enough oxygen is present to form ordered stoichiometric oxides.

Following an oxygen exposure of 500 L evidence of SnO-like loss features are observed. This can be seen in the $E_p = 100$ eV spectrum of figure 5-7 in which the feature at 9 eV is present and the loss feature at 27.5 eV has sharpened. Also, in the $E_p = 200$ eV spectrum seen in figure 5-7 a very weak shoulder at 9 eV is present, and the Sn 4d feature has sharpened with respect to the $E_p = 200$ eV 100 L and clean spectra. The combined presence of the surface plasmon loss feature from both metal and SnO suggests that oxide island formation may occur as proposed by Bevolo et al. (85). As the primary beam energy is increased to 400 and 600 eV, features associated with SnO decrease in prominence, yet their presence can still be seen. It is not believed that SnO is present to the depths probed using the 400 and 600 eV beams, but that the SnO features in these spectra are associated with the near surface region which is also probed using the higher beam energies.

The outermost 3 nm are observed to saturate for low-pressure exposures following a dose of 1500 L. This is observed by comparing figures 5-8 and 5-9. The spectra for all the primary beam energies used are essentially identical. In contrast, using AES and XPS a

saturation exposure of between 2000 and 3000 L is observed (87,94). Thus, although the outer 3 nm have saturated, oxygen diffuses through this layer and continues to oxidize the metal beneath it following exposures greater than 1500 L. The depth of the SnO layer formed following a saturation exposure appears to lie between the sampling depth of the 200 and 400 eV beams and thus is approximately 2 nm thick. The decrease in oxidation state from +2 is observed in figure 5-8 by the broadening of the Sn 4d loss feature in the $E_p = 400$ eV spectrum. Moreover, the intensity of the 14 eV peak relative to the 9 eV shoulder in the $E_p = 400$ eV spectrum is much greater than expected based on the behavior of plasmon excitations with varying probed depth. It is possible that the metal bulk plasmon excitation is contributing to the 14 eV peak intensity. Further evidence for the 2 nm depth of the SnO-like layer can be found from figure 5-12. In the lower spectrum, the most bulk sensitive, the sampling depth is similar to the $E_p = 400$ eV spectrum of figure 5-8. In agreement with figure 5-8 the Sn 4d loss feature broadens relative to that in the two more surface sensitive spectra providing evidence for a decrease in the oxidation state.

As stated earlier, following high-pressure exposures, a wide range of oxidation states are present. Loss spectra following exposures at high pressure are shown in figures 5-15 and 5-16. Figure 5-15 was obtained following a dose of 160 Torr of oxygen for 5 minutes, and figure 5-16 was obtained following air exposure for 5 minutes. The exposure of 160 Torr was chosen because it is approximately the partial pressure of oxygen in air. In both figures

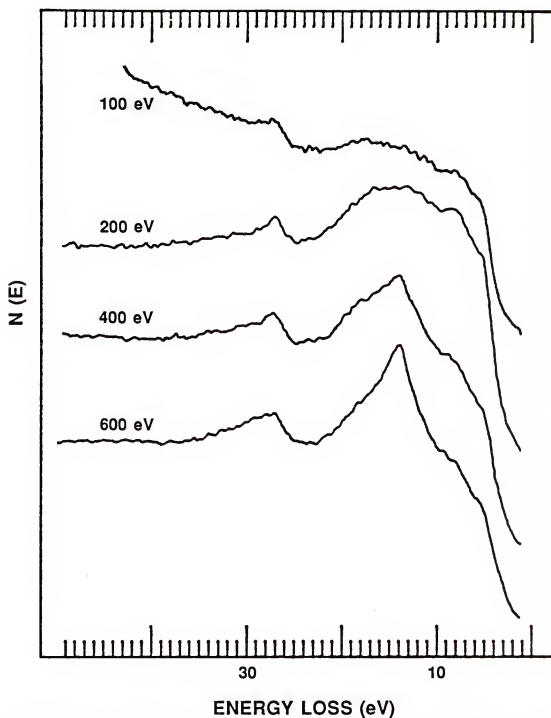


Figure 5-15. ELS spectra obtained from polycrystalline tin following an oxygen exposure of 160 Torr for 5 minutes. The primary beam energies used are 100, 200, 400 and 600 eV.

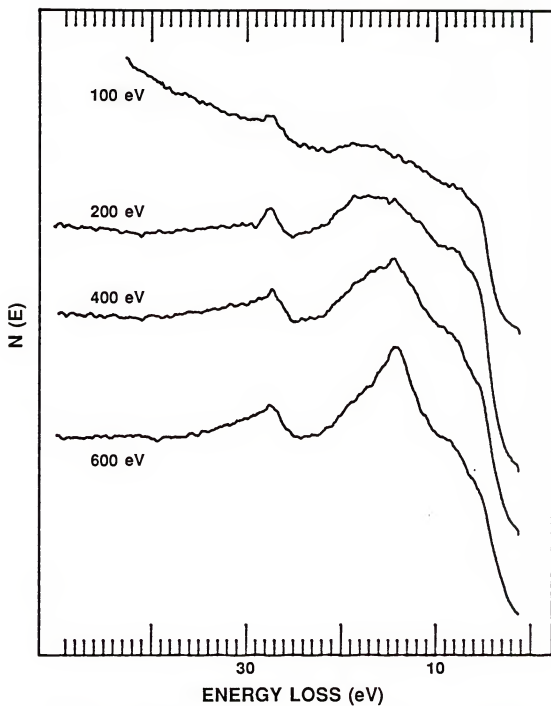


Figure 5-16. ELS spectra obtained from polycrystalline tin following air exposure for 5 minutes. The primary beam energies used are 100, 200, 400 and 600 eV.

5-15 and 5-16 features characteristic of SnO and SnO₂ at 14 and 20 eV respectively are observed throughout the probed surface region. From both figures it appears that a maximum contribution of SnO₂ loss features occurs at the depth probed by the 200 eV beam or approximately 1.5 nm. Also, the air-exposed surface appears to have a greater concentration of SnO₂ at this depth. It is evident though that at no depth does SnO₂ dominate the spectra. Because a metal contribution to both $E_p = 600$ eV spectra is observed, the depth of the oxide layer formed following either exposure is approximately 3 nm. This is clear from the broadening of the Sn 4d feature and the strong, sharp peak at 14 eV which is probably due in part to the metal bulk-plasmon excitation. Also, no distinct loss feature is observed at 24.5 eV resulting from hydroxyl formation (99) on the air-exposed surface. Based on the above results, a semiquantitative ELS depth profile of the surface region of sputtered polycrystalline tin as a function of oxygen exposure is presented in figure 5-17. In figure 5-17 the average overall oxidation state is plotted. The oxidation state following a 100 L exposure is only tentatively drawn.

Conclusions

An extensive and detailed ELS investigation of clean and oxygen-exposed polycrystalline tin has been completed. A description is presented for determining the depth probed using various primary beam energies and experimental geometries with ELS. Firm evidence of multiple plasmon excitations from the cleaned surface have been observed. Also, evidence of surface roughness caused by sputtering

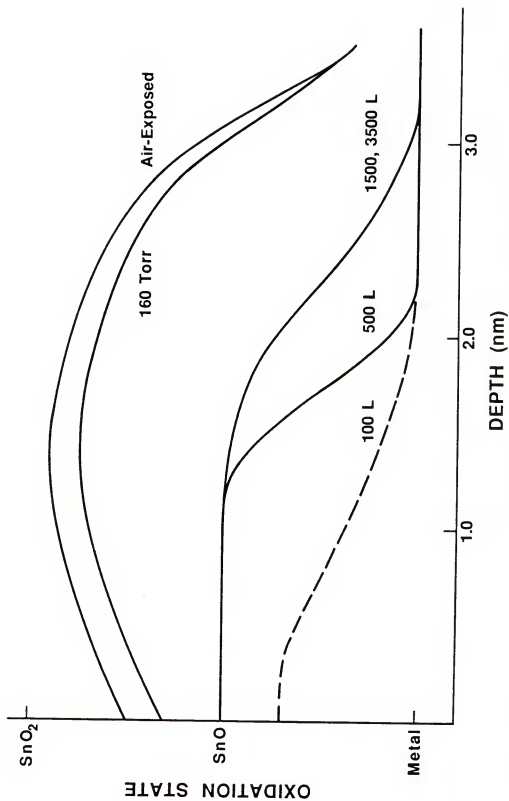


Figure 5-17. An ELS semiquantitative depth profile of sputtered polycrystalline tin as a function of oxygen exposure.

has been observed using a 100 eV primary beam energy. Following oxygen adsorption, evidence of a decrease in surface roughness seems to occur.

No evidence of either SnO or SnO₂ is observed following oxygen exposures of 100 L or less. Following an exposure of 500 L, there is some evidence that an SnO-like near surface layer is present. The outermost 3 nm are observed to saturate, and the outermost 2 nm layer is approximated by SnO following an exposure of 1500 L. Using AES and XPS a saturation exposure between 2000 and 3000 L is determined (87,94), thus oxygen must continue to diffuse through the outermost 3 nm and oxidize the metal beneath it following exposures greater than 1500 L. No distinct evidence of SnO₂ is observed following any low-pressure oxygen exposure. Also, using angle-resolved ELS clear evidence is provided for the main loss peaks of SnO at 14 eV and 9 eV being derived from a bulk and a surface plasmon excitation respectively. Following high-pressure exposures a broad mixture of oxidation states are present throughout the surface region. Lower oxidation states appear to dominate following these exposures, however, some SnO₂ is observed and is at a maximum near 1.5 nm in depth. Approximately a 3 nm oxide layer is formed following either a 160 Torr oxygen or air exposure.

CHAPTER VI
AN ENERGY-RESOLVED ELECTRON STIMULATED DESORPTION (ESD)
STUDY OF OXYGEN-EXPOSED Ag(110)

INTRODUCTION

The interaction of oxygen and silver has received much attention due to the high catalytic activity of silver for the selective epoxidation of ethylene (100-108). There has also been a great deal of interest in the model interaction of oxygen with Ag(110)(109-125). In fact, it has been shown that the Ag(110) surface is 100 fold more active for the epoxidation of ethylene per surface atom than the actual industrial catalyst (120).

Adsorbed oxygen on the Ag(110) surface has been studied using many surface analytical techniques including XPS, (116), UPS, (116, 118, 125) high resolution electron energy loss spectroscopy (HREELS), (114, 117, 124) TPD, (111-115, 117), LEED (109-112, 117, 122-124) and ISS (110, 130). Several of these studies have determined an initial sticking coefficient of about 10^{-3} at 300 K. The initial sticking coefficient is also found to decrease with increasing temperature providing evidence of a precursor state for oxygen chemisorption (111, 125). In addition to a possible precursor state, the formation of three adsorbed states of oxygen have been proposed: an adsorbed dioxygen state, a subsurface dissociated oxygen state and an adsorbed dissociated oxygen state. The dioxygen state has been most commonly observed at temperatures below 120 K and produces a 1x1 LEED pattern (114, 123). It has also been proposed that a dioxygen adsorbed state

exists at 473 K following oxygen exposures at pressures greater than 0.1 Torr (115, 116). However, it is not clear if these two dioxygen states are the same. The subsurface oxygen has been shown to interchange easily with the surface oxygen (114, 115, 117), but the surface-subsurface oxygen interaction has not been well characterized. Backx et al. (114) have also shown that this subsurface oxygen is stable at temperatures up to 725 K. The dissociated oxygen state has been the most studied of the three states. It is formed by exposure to oxygen at temperatures above 170 K or by heating a previously oxygen-exposed surface above 170 K (116). Oxygen thermally desorbs from this state with a maximum near 570 K (115).

The use of ESD to study the oxygen-silver system has received little attention. An ESDIAD (electron stimulated desorption ion angular distribution) study of oxygen on silver(110) has been presented by Bange et al. (123). They used the desorbing ion angular distribution in an attempt to determine the geometry of the surface O-Ag bond, but their results do not agree with HREELS (114, 115, 124) or surface enhanced X-ray adsorption fine structure data (121).

The emphasis of the present study is to determine the composition and the energy distributions of the positive ions desorbing from oxygen-exposed Ag(110) rather than focusing on the state of the adsorbed oxygen. The motivation for this study is that it may be possible to produce a hyperthermal oxygen atom beam source using ESD. This type of source would be useful in studying collision dynamics and in materials research. In this source oxygen would

diffuse from a high pressure region through a metal membrane and desorb under electron bombardment at the metal surface. Silver is a candidate for the metal membrane because oxygen readily diffuses through it (5). This work is part of an ongoing effort to obtain the information required to construct an oxygen atom source. A previous part of this study by Outlaw et al. (5) presented a technique for detecting and studying neutral desorption from oxygen-exposed polycrystalline silver.

Experimental Procedure

The ultrahigh vacuum apparatus used in this study has been described previously (45). The base pressure in the vacuum system during these experiments was 2×10^{-10} Torr. The silver sample was a single crystalline disk cut in the (110) orientation with a purity of 99.999%. The crystal was mechanically polished followed by solvent cleaning prior to insertion into the vacuum system. It was then cleaned by annealing at 1125 K followed by repeated 500 eV argon ion etching and low temperature annealing at 625 K. Heating was done using a tungsten filament placed directly behind the sample. The major contaminant was sulfur. Using AES and ISS, sulfur was observed to segregate to the surface at appreciable rates above 800 K. Surface cleanliness was monitored carefully throughout the study using AES, ISS and LEED. Oxygen exposures were done at room temperature.

LEED patterns were observed using a PHI Model 15-180 hemispherical grid system. The AES, ESD and ISS data were obtained

using a double-pass cylindrical mirror analyzer (CMA) (PHI Model 15-255 GAR) with the sample positioned at an angle of 45° with respect to the CMA axis. AES and ISS data were taken by operating the CMA in the nonretarding mode. The details of the data collection for these two techniques are given elsewhere (126). ESD data were taken in both a total ion detection mode and in a time-gated ion detection mode (127) (ion refers to positive ions only throughout the paper). In both modes the CMA was operated in the retarding mode using pulse counting (46) with a pass energy of 80 eV ($\Delta E/E_{\text{pass}} = 0.016$). The front grids of the CMA were held at a potential of -80 volts relative to the sample in order to accelerate the ions. The time-gated mode allowed the CMA to function as a time-of-flight mass spectrometer (127, 128). In this mode both mass/charge (m/e) spectra and $N(E)$ spectra for a particular m/e ratio were obtained. Mass analysis was achieved by pulsing the electron beam onto the sample for 300 ns using the electron gun deflector plates, waiting a prescribed length of time (e.g. $5.5 \mu\text{s}$ for H^+) and then pulse counting for 300 ns. The angle resolving aperture in the CMA which selects 12° out of the possible 360° was positioned so as to obtain the maximum signal for all ESD experiments. A primary beam current of 500 nA was used for the ESD experiments, and a beam energy of 220 eV was used for the time-gated experiments. The ESD results presented below were reproduced many times throughout the study.

Results and Discussion

ESD spectroscopy of ions is sensitive to the outermost layer of atoms due to the large probability that ions excited to an antibonding state beneath the surface are recaptured or neutralized before desorbing. ESD may be sensitive to species desorbing from impurities as well as species desorbing from minority and/or defect sites on the surface. Both ISS and AES were used in this study to monitor the surface cleanliness. It is difficult, however, to determine if the ions desorbing originate from symmetrical bonding sites of the ordered surface or from minority and/or defect sites on the surface. Although a determination of surface sites active for ESD would be of interest, it is not the primary emphasis of this study. However, it is important to know if a relationship exists between the surface preparation and the desorption products or energy distributions. A previous study was performed in this laboratory using an unpolished Ag(110) surface. Although no LEED pattern could be obtained from this surface, energy distributions similar to those presented here were observed. Thus, surface roughness does not seem to affect the ion energy distribution in this case, but further studies of sputtered and polycrystalline surfaces would be useful and are in progress.

An ISS spectrum obtained from the cleaned surface (repeatedly sputtered and annealed) is shown in figure 6-1. The large peak near $E/E_0 = 0.9$ is due to silver, and the very small feature near $E/E_0 = 0.6$ is due to oxygen. No other ISS features are observed. ISS is sensitive to essentially the outermost atomic layer because an ion

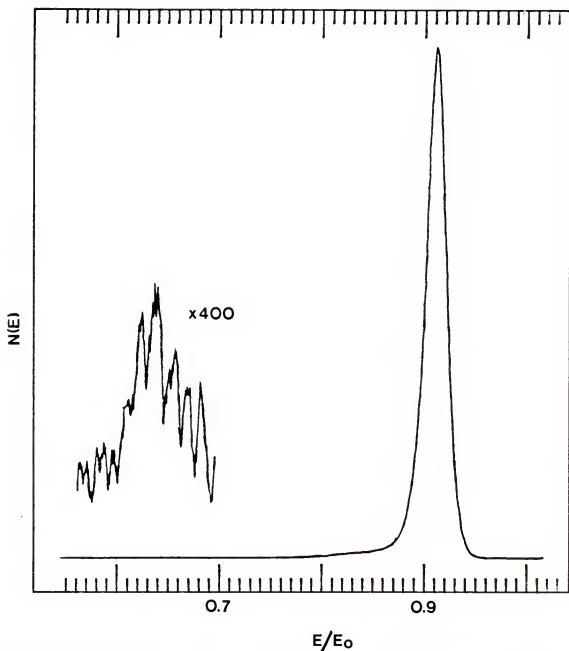


Figure 6-1. An ISS spectrum taken from the cleaned silver surface.

which penetrates beneath the surface has a high probability of either being neutralized or scattered inelastically. In figure 6-1 the ratio of the oxygen to silver peak heights is 0.001. Based on an expression for ISS cross sections given by Parilis (129) the ratio of the silver to oxygen cross sections is approximately 4. Thus, less than a hundredth of a monolayer of oxygen is present on the cleaned surface.

An AES spectrum of the cleaned surface is shown in figure 6-2. An O(KLL) to Ag(MNN) peak-to-peak height ratio of 0.05 is found, and it was not possible to reduce this ratio further using repeated sputtering and annealing cycles. Since AES is less surface sensitive than ISS, this oxygen must lie beneath the surface.

ESD was also performed on the cleaned surface in an effort to detect the small amount of oxygen found using ISS. Using ESD, no oxygen or oxygen-containing species were detected. Only small amounts of hydrogen were found to desorb from the cleaned surface.

ESD ion energy distributions corresponding to different stages of the initial oxidation immediately following the sample cleaning are given in figure 6-3. Spectrum 6-3(a) was obtained following three exposures of oxygen, one of 3000 L followed by two of 6000 L. The sample was heated to 625 K between each dose since heating to 625 K results in the thermal desorption of the surface oxygen but does not remove the subsurface oxygen (114, 115, 117). Following two more exposures of oxygen, one of 3000 L and a second of 6000 L with heating to 625 K between them, spectrum 6-3(b) was obtained. In this spectrum an increase in the relative desorption yield of ions with a

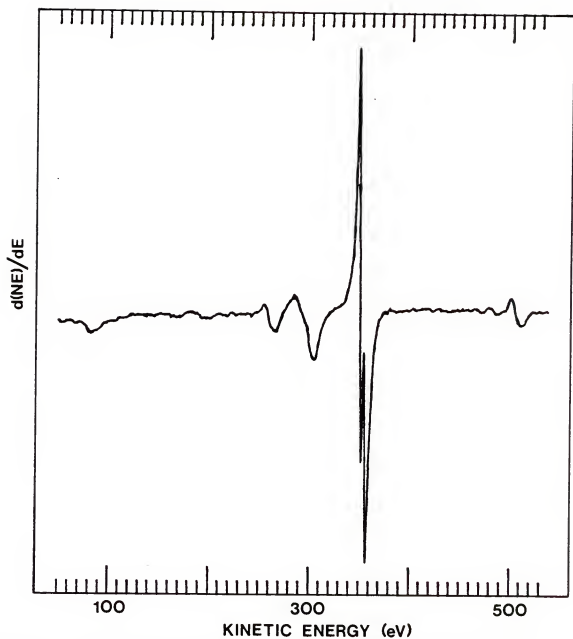


Figure 6-2. A typical AES spectrum taken from the cleaned silver surface.

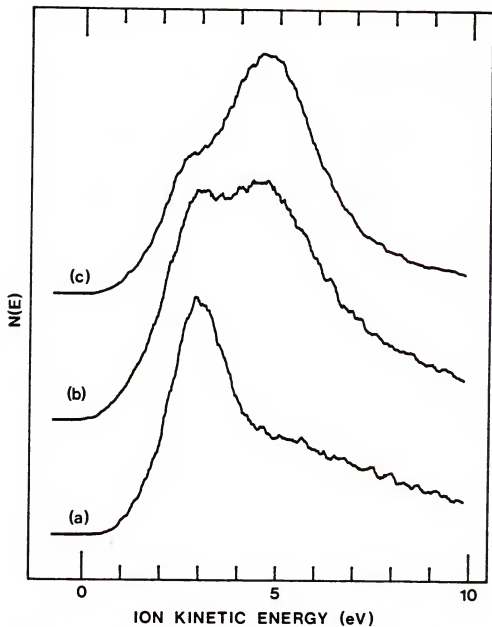


Figure 6-3. Total ion energy distributions obtained during the initial oxygen exposures. From spectrum (a) to (c) the subsurface oxygen concentration is increasing. A primary beam energy of 300 eV was used to obtain these spectra. The ordinates are not scaled relatively to each other.

kinetic energy of 4.5 eV is seen relative to that shown in 6-3(a). Spectrum 6-3(c), which shows the desorption of substantially more ions with a kinetic energy of 4.5 eV than observed in either 6-3(a) or 6-3(b), was obtained following heating of the sample to 625 K again and a subsequent dose of 7000 L. The total ion energy distributions do not vary appreciably from spectrum 6-3(c) following further sample heating to 625 K and subsequent oxygen exposures.

In order to determine the compositions of the ions which desorb with kinetic energies of 3.0 and 4.5 eV, ESD mass analysis was performed. Two time-gated ESD spectra are presented in figure 6-4. Figure 6-4(a) is a spectrum showing those ions which desorb with a kinetic energy of 3.2 eV, and figure 6-4(b) is a spectrum showing those ions which desorb with a kinetic energy of 4.7 eV. Based on a flight time analysis, the peak at 5.5 μsec is due to hydrogen and a peak at 18.4 μsec is due to oxygen desorbing as a hydroxide ion. Atomic oxygen ions are also found to desorb with a flight time of 16.8 μsec as shown below. It is clear from figure 6-4 that more OH^+ desorbs relative to H^+ when the detected ion energy is 4.7 eV. ESD energy distributions of OH^+ and H^+ are given in figure 6-5. In agreement with figure 6-4, OH^+ desorbs with an energy of 4.5 eV, and H^+ desorbs with an energy of 3.0 eV. Only one peak in the energy distributions of either OH^+ or H^+ is observed following any heat treatment or oxygen exposure.

Based on the results presented in figures 6-3 through 6-5, it appears that the sites from which oxygen-containing species desorb do not fill initially upon oxygen exposure. This may imply that the

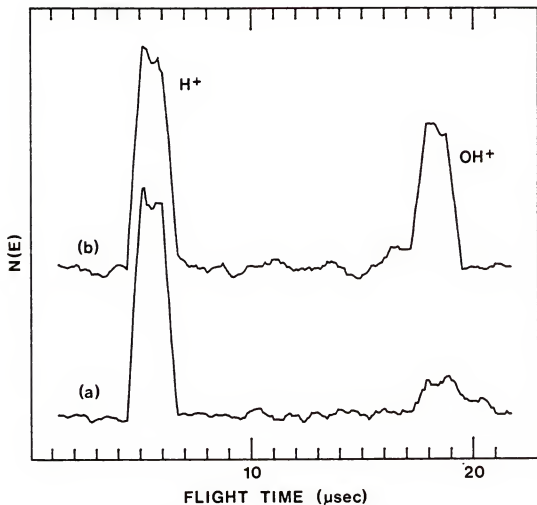


Figure 6-4. ESD mass spectra obtained from Ag(110) following the initial oxygen exposures. Spectrum (a) was obtained by collecting ions with an energy of 3.2 eV, and spectrum (b) was obtained by collecting ions with an energy of 4.7 eV. The ordinates are not scaled relatively to each other.

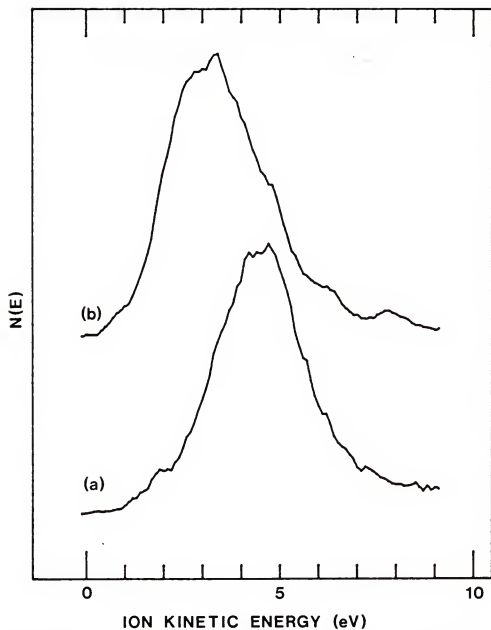


Figure 6-5. Time-gated energy distributions for (a) OH^+ and (b) H^+ .

subsurface oxygen bonding sites fill first and that the subsurface oxygen detected initially using AES is not representative of an oxygen-saturated subsurface region. This behavior is consistent with a recently completed ISS and angle-resolved AES study of oxygen adsorption on polycrystalline silver (130). The ESD data shown in this paper probably is representative of that which would be obtained from a working oxygen atom source since the subsurface region would be filled with oxygen due to transport of oxygen through the membrane.

The effect of prolonged exposure of the surface to an electron beam is shown in figure 6-6. Also presented is the effect of annealing the sample at 625 K on the energy distribution. Three total ion energy distributions are depicted. Spectrum 6-6(a) is the familiar energy distribution obtained following the initial oxygen exposures as well as an additional 7500 L exposure. Both hydrogen and hydroxide ions are evident. Exposing this surface to a 220 eV electron beam of 1.2 μ A over a diameter of about 0.2 mm for 25 minutes alters the energy distribution to that shown in figure 6-6(b). The overall signal has decreased by a factor of 3, and the hydrogen ion contribution to the spectrum at 3.0 eV kinetic energy has been greatly reduced. This suggests that hydrogen has a greater cross section for desorption than oxygen (hydroxide) on the Ag(110) surface. The electron beamed surface was then annealed at 625 K for 10 minutes, and the resulting energy distribution is shown in figure 6-6(c). The overall signal has been further reduced by a factor of 2, but no significant change in the energy distribution is

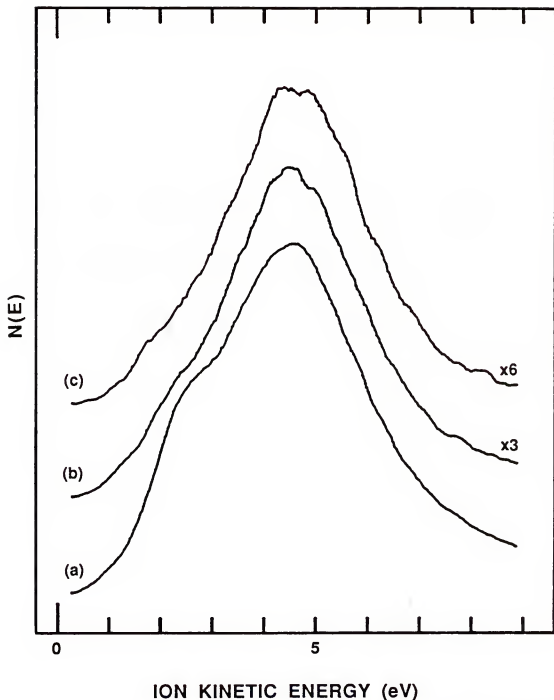


Figure 6-6. Total ion energy distribution curves. Spectrum (a) was obtained following the initial oxygen exposures and an additional 7500 L. Spectrum (b) was obtained following prolonged exposure to the electron beam. Spectrum (c) was obtained by annealing the surface at 625 K. The ordinates are scaled as shown.

observed. The reduction in the signal following annealing is expected based on the results of numerous TPD studies (111-115, 117). In fact, a more marked reduction in signal was anticipated. The fact that the signal did not decrease dramatically may be due to subsurface oxygen migrating to the surface during the anneal and repopulating some of the surface sites.

Although the surface oxygen seems to desorb predominately as a hydroxyl species, an atomic oxygen species is also found to desorb following low oxygen exposures. This can be seen in figure 6-7 which shows three spectra (ion kinetic energy of 4.7 eV) obtained following oxygen doses of 250, 500 and 1000 L. The sample was annealed at 625 K between each exposure. It is evident that the O^+ desorption decreases relative to OH^+ desorption as the oxygen exposure increases. This suggests the possibility of at least two binding sites for oxygen on the Ag(110) surface and that the site from which atomic oxygen desorbs seems to fill first upon oxygen exposure. Another possibility is that larger oxygen exposures cause more hydrogen to be attracted to the surface region to form hydroxyl groups. This would also explain the growth of the H^+ desorption peak.

In addition to a variation in ion desorption distributions with exposure, a variation of the total ion energy distribution with primary beam energy is observed. The total ion energy distribution changes significantly upon varying the primary beam energy from 300 to 400 eV. As seen in figure 6-8, the relative OH^+ desorption yield is decreased by changing the primary beam energy from 300 to 400 eV

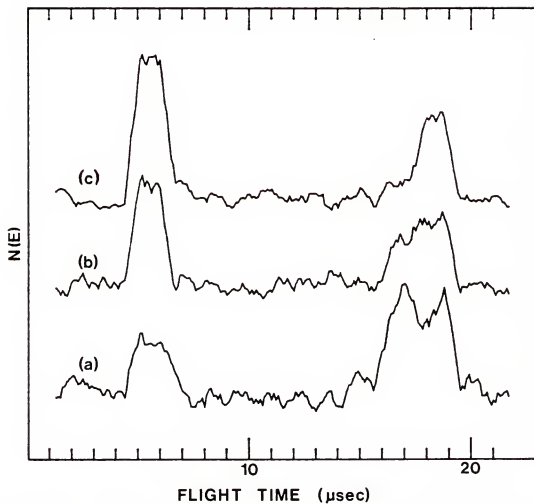


Figure 6-7. Mass spectra of ions collected with an energy of 4.7 eV as a function of oxygen exposure: (a) 250 L, (b) 500 L and (c) 1000 L. The ordinates are not scaled relatively to each other.

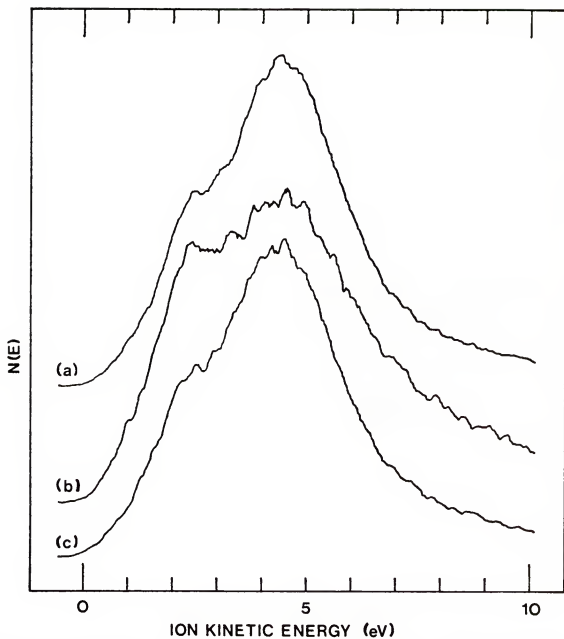


Figure 6-8. Total ion energy distributions obtained successively with primary beam energies of (a) 300, (b) 400 and (c) 300 eV. The ordinates are scaled such that (b) has been expanded by a factor of two.

whereas the H^+ desorption yield increases slightly upon increasing the beam energy to 400 eV. Also, the energy distribution resulting from the 400 eV beam is wider particularly on the high-energy side. This suggests that, combined with changes in the ion desorption yields, other desorption mechanisms for both hydrogen and oxygen may be present. Very little deviation in the total ion energy distribution is observed upon varying the primary beam energy between 100 and 300 eV or 400 and 600 eV. The difference between the 300 eV and 400 eV experiments is that Ag 3d core holes are created using a 400 eV primary beam energy. One of the possible decay mechanisms of the Ag 3d core hole involves an Auger process that leaves two final state holes in the Ag 4d valence band. It is likely that this Auger process alters the silver-oxygen and silver-hydrogen bonds and possibly the oxygen-hydrogen bond. The actual mechanisms through which the Auger process influences the observed ESD behavior is not understood very well.

The slight increase in the hydrogen desorption yield is difficult to interpret because the relative amount of hydrogen bonded to silver compared to hydrogen bonded to oxygen is unknown. The difficulty in determining the relative amount of hydrogen bonded to silver versus oxygen can be seen by comparing figure 6-8 with the spectrum shown in figure 6-3(a). From figure 6-8 it is seen that the amount of hydrogen desorbing decreases with decreasing oxygen dosage. Furthermore, when both surface and subsurface oxygen are removed by heating to 1125 K, the total ion desorption count rate becomes extremely small. These two observations indicate that the

surface hydrogen is associated with adsorbed oxygen. Conversely, from the spectrum shown in figure 6-3(a), which was obtained before the surface region had been saturated with oxygen, more H^+ desorbs relative to OH^+ suggesting that hydrogen may also bond directly to silver on the surface. The hydrogen signal does not decrease to the extent that O^+ becomes the predominant desorbing oxygen species relative to OH^+ .

The appearance of desorbing hydrogen and hydrogen-containing species is not unexpected. Hydrogen-containing species have been found to desorb from zirconium (1), gallium arsenide (131) and many other surfaces (127) even though the surfaces were not predosed with hydrogen in many cases. In the previous part of this study (5), hydrogen atoms were found to desorb from polycrystalline Ag with no hydrogen predosing. In this study the amount of desorbing hydrogen was gradually depleted following many sample anneals, but the hydrogen could not be completely eliminated. Hydrogen is moderately soluble in Ag (132, 133), and it is believed that the origin of the desorbing H^+ is from hydrogen dissolved in the bulk silver. If it were originating from the background gases, the hydrogen ESD signal would not continually decrease with prolonged sample annealing.

Conclusions

Adsorbed oxygen on the Ag(110) surface predominately desorbs by ESD as a hydroxyl ion. The hydrogen which desorbs originates from the bulk silver and is probably bonded both to silver and to oxygen on the surface. OH^+ is found to desorb with an energy of 4.5 eV, and

H^+ desorbs with an energy of 3.0 eV. Two or more possible binding sites for oxygen exist on the Ag(110) surface. Exciting the Ag 3d core levels is observed to dramatically affect the desorption yield of OH^+ and H^+ and the energy distributions of these ions. This effect may be due to the $M_{4,5}N_{4,5}N_{4,5}$ silver Auger transition which is one decay mechanism of a Ag 3d core hole.

CHAPTER VII
GENERAL CONCLUSIONS AND
RECOMMENDATIONS FOR FUTURE RESEARCH

The oxidation of polycrystalline zirconium has been studied using a variety of surface spectroscopic techniques. The initial adsorption of oxygen was followed by using ISS, AES and XPS. These three spectroscopies allow for the surface region to be probed to differing depths. ISS is sensitive to essentially the outermost layer only. Further, for zirconium, AES is more surface sensitive than XPS because the dominate zirconium Auger electrons have a kinetic energy of less than 180 eV, but the Zr 3d photoelectrons have a kinetic energy of greater than 1080 eV when using a magnesium anode. Based on the results from these three spectroscopies, it is determined that the adsorption of oxygen proceeds by first populating some of the outermost binding sites followed by transport of oxygen into the subsurface region. Moreover, before the surface binding sites are saturated and following an exposure of approximately $3/4$ L, most of the oxygen which adsorbs migrates into and oxidizes the subsurface region. The abrupt change in the rate of surface population versus subsurface population at about a $3/4$ L exposure is believed to be caused by the formation of an oxide lattice which more readily allows the transport of oxygen to the subsurface. This implies that oxygen would rather lie beneath the surface. The surface sites are found to saturate following an oxygen dose of 6 L, and a 40 to 50 L exposure results in saturation of the surface region.

ELS has also been used to study an oxygen-exposed zirconium surface. The loss spectra for clean and oxygen-exposed polycrystalline zirconium have been interpreted in terms of a density-of-states model. All major loss features have been identified as either collective mode excitations (plasma oscillations) or electronic transitions. Based on this interpretation the angular momentum character and the binding energies of the unoccupied levels of clean and partially oxidized zirconium have been determined. The energies of the lower unoccupied levels of clean zirconium characterized here using ELS agree well with those determined using bremsstrahlung spectroscopy (28), and the energy and angular momenta of the levels agree with those obtained using theoretical methods (28,48). The higher lying unoccupied levels of clean zirconium and all but the lowest unoccupied levels of oxygen-exposed zirconium characterized here using ELS have not been presented in the literature previously.

The oxidation state of a 40 L oxygen-dosed zirconium surface is found to increase with depth. Evidence for a ZrO -like states in the first five atomic layers in depth is observed. Beneath this surface region, Zr_2O_3 -like states are observed in the next five to eight atomic layers. The oxidation state appears to vary continuously with depth suggesting the presence of nonstoichiometric oxides. The combined use of ISS, AES, XPS and ELS have led to a good understanding of the initial oxidation of zirconium.

Additionally, the interaction of hydrogen with zirconium has been studied using ELS. Few surface spectroscopies are sensitive to

the presence of hydrogen, and even fewer are sensitive to subsurface hydrogen. However, ELS is sensitive to hydrogen throughout the surface region because ELS features depend on both the filled and unfilled density of states. A detailed interpretation of the first electron-energy-loss data of hydrogen-exposed and hydrogen-exposed/oxygen-exposed polycrystalline zirconium has been completed. Following a 2000 L dose of hydrogen at 770 K, the depth of the hydrided layer was determined to be between 3 and 4 nm. It was also determined that both a hydride and an oxide species may be present in the surface region following exposure of oxygen to a hydrogen-predosed surface. Differences in the ELS spectra taken from an oxygen-dosed zirconium surface and an oxygen- and hydrogen-dosed zirconium surface suggest that less oxygen adsorbs on a hydrogen-predosed surface and/or the adsorbed oxygen interacts less with the zirconium due to an interaction with hydrogen.

An extensive and detailed ELS investigation of clean and oxygen-exposed polycrystalline tin has also been completed. A description is presented for determining the depth probed using various primary beam energies and experimental geometries using ELS. Firm evidence of multiple plasmon excitations from the cleaned surface have been observed. Also, evidence of surface roughness caused by sputtering has been observed using a 100 eV primary beam energy. Following oxygen adsorption, evidence of a decrease in surface roughness seems to occur.

No evidence of stoichiometric oxides are observed following oxygen exposures of 100 L or less. Following an exposure of 500 L,

some evidence that an SnO-like near surface layer is present. The outermost 3 nm are observed to saturate following an exposure of 1500 L; however using AES and XPS a saturation exposure between 2000 and 3000 L is determined (87,94). Thus, following exposures greater than 1500 L, oxygen must continue to diffuse through the outermost 3 nm and oxidize the metal beneath it. No distinct evidence of SnO₂ is observed following any low-pressure oxygen exposure. Roughly a 2 nm oxide layer approximated by SnO is formed following a 1500 L oxygen dose. Also, using angle-resolved ELS, clear evidence is provided for the main loss peaks of SnO at 14 eV and 9 eV being derived from a bulk and a surface plasmon excitation respectively. Following high pressure exposures a broad mixture of oxidation states is present throughout the surface region. Although lower oxidation states appear to dominate, some SnO₂ is observed and is at a maximum near 1.5 nm in depth. Approximately a 3 nm oxide layer is formed following either a 160 Torr oxygen or air exposure.

It is clear that a better understanding of the Zr-O-H interaction and/or the Sn-O interaction can be gained from a better understanding of ELS. Due to the difficulty in knowing the unoccupied energy levels during initial adsorption processes assignments of ELS features are difficult to make. A solution to this problem can be obtained from the use of inverse photoemission spectroscopy (IPS). Using IPS the density of unoccupied levels can be determined as a function of exposure.. Thus, combining UPS or valence band XPS with IPS allows for the characterization of the joint density of states near the Fermi level thereby greatly aiding the task of interpreting ELS spectra.

An energy-resolved ESD study of the interreaction of oxygen with the Ag(110) has also been completed. Adsorbed oxygen on the surface is found to desorb by ESD as a hydroxyl ion. The hydrogen which desorbs originates from the bulk silver and is probably bonded both to silver and oxygen on the surface. OH^+ is found to desorb with an energy of 4.5 eV, and H^+ desorbs with an energy of 3.0 eV. Evidence is also found for two or more possible binding sites for oxygen on the Ag(110) surface. Exciting the Ag 3d core levels is observed to dramatically affect the desorption yield of OH^+ and H^+ and the energy distributions of these ions. This effect may be due to the $\text{M}_{4,5}\text{N}_{4,5}\text{N}_{4,5}$ silver Auger transition which is one decay mechanism of a Ag 3d core hole.

A better understanding of the Ag-O interaction can be gained from combining with ESD the use of other highly surface sensitive spectroscopies such as angle-resolved AES (ARAES), angle-resolved XPS (ARXPS) and ISS. It would be useful to relate ESD behavior with surface oxygen concentration which could be obtained using ISS. In addition, a better understanding of the surface-subsurface oxygen interaction could be obtained using ARAES and ISS. It would also be interesting to expose silver to high pressure oxygen at high temperature in an effort to form bulk silver oxides. These silver oxides could then be characterized using AES, XPS and perhaps ELS. With an understanding of these results it may then be possible to determine the unknown chemical and electronic state of the silver following low-pressure and low-temperature, high-pressure oxygen exposures.

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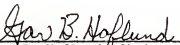
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BIOGRAPHICAL SKETCH

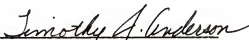
Gregory Richard Corallo was born in Livermore, California, on February 14, 1961. He is the son of Richard Corallo and Patti Schall and has one older sister, Cathe. Gregory was married to the former Cheryl Lee Fox on September 1, 1984. They have no children, but do have one cat named Auger.

Gregory was raised in Livermore, California, a town approximately 50 miles east of San Francisco, where he attended school and graduated from Granada High School in 1979. He then entered the University of California at Davis in September of 1979 and, after partying for four years, received a Bachelor of Science degree in chemical engineering in September of 1983. Gregory entered graduate school in chemical engineering at the University of Florida in the fall of 1983 and received a Master of Science degree in fall, 1984. He continued in the Ph.D. program at the University of Florida where he has been until the present.

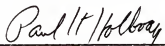
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Science and Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1987

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